Supplementary Information

Selective Monophosphorylation of Cyclic Diols and Polyols *via* Hemiboronic Acid Catalysis

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1. General Information

The following supporting information contains representative experimental procedures and details for the isolation and characterization of compounds. Full characterization of all novel compounds and partial characterization of known compounds are described. All reactions were performed in regular glassware with no exclusion of air or moisture unless otherwise noted. 2-formylphenylboronic acid was purchased from Ambeed and recrystallized from hot H_2O prior to use. Hydroxylamine (50 wt. % solution in water) was purchased from Sigma-Aldrich and used as received. Diethyl chlorophosphate was purchased from Sigma-Aldrich and used as received. Diisopropylethylamine was purchased from Sigma-Aldrich and used as received. All solvents were purchased as ACS reagent grade and used as received, unless otherwise noted. All other chemicals were purchased from commercial suppliers and used as received. Thin layer chromatography was performed on Supelco glass silica gel 60 F_{254} plates, which were visualized under UV light and with KMnO4 stain. Column chromatographic separations were performed on silica gel 60 using ACS grade hexanes, ethyl acetate, acetone, and dichloromethane as eluents.

NMR spectra were recorded at ambient temperature using Agilent/Varian DD2 MR two channel 400 MHz, Bruker Avance NEO two channel 400 MHz, Bruker Avance NEO 3-Channel 500 MHz, Agilent VNMRS four-channel, dual receiver 700 MHz, and Bruker Avance NEO 3-Channel Console 800 MHz, with spectrometers operating at the indicated frequency for ^1H NMR. All NMR chemical shifts are reported in ppm (δ) units with residual solvent peaks ($CDCl_3$, CD_3CN, Acetone-d_6, CD_3OD, or D_2O) as the internal reference. NMR data is reported using the following abbreviations: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; p, pentet; h, hextet; hept, heptet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; ddd, doublet of doublet of doublets; dddd, doublet of doublet of doublet of doublets; app, apparent; m, multiplet. The error of coupling constants from ^1H NMR spectra is estimated to be approximately 0.3 Hz. The quaternary carbon bound to boron is often not observed due to the quadrupolar relaxation of boron, which was the case for all boron-containing compounds herein. An OHAUS a-AB23PH Aquasearcher pH meter with ST230 pH probe was used for pH measurements. High resolution mass spectra were recorded by the University of Alberta Mass Spectrometry Services Laboratory using either electron impact (EI) or electrospray (ESI) techniques. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Nicolet 8700 FTIR Spectrometer and Continuum FTIR Microscope, MCT detector and XT-KBR Beamsplitter.

2. Reaction Optimization

2.1. Screening of Hemiboronic Acid Catalysts

2.1.1. Synthesis of Screened Hemiboronic Acid Catalysts

Catalysts **BAC 1a**[1], **BAC 2**[1], **BAC 3**[2], **BAC 4**[1], **BAC 5**[3], **BAC 6**[4], **BAC 7**[4] were synthesized as has been previously described. **BAC 8** and **BAC 9** were purchased from Combi-Blocks, Inc. and Ambeed, respectively, and used as received.

2.2. Screening of Phosphorylating Agents

2.2.1. Synthesis of Screened Phosphorylating Agents

Diethylchlorophosphate, dimethylchlorophosphate, diphenylchlorophosphate, tetrabenzylpyrophosphate, and 2-cyanoethyl *N,N*-diisopropylchlorophosphoramidite were purchased from Sigma-Aldrich, and used as received. Dibenzylchlorophosphate was prepared as previously described.[5]

2.2.2. Diphenylchlorophosphate – Product Cyclization

Upon purification of the product obtained *via* phosphorylation with diphenylchlorophosphate, it was observed that the product had cyclized to give a symmetrical cyclic phosphate, as evidenced by ^{1}H NMR.

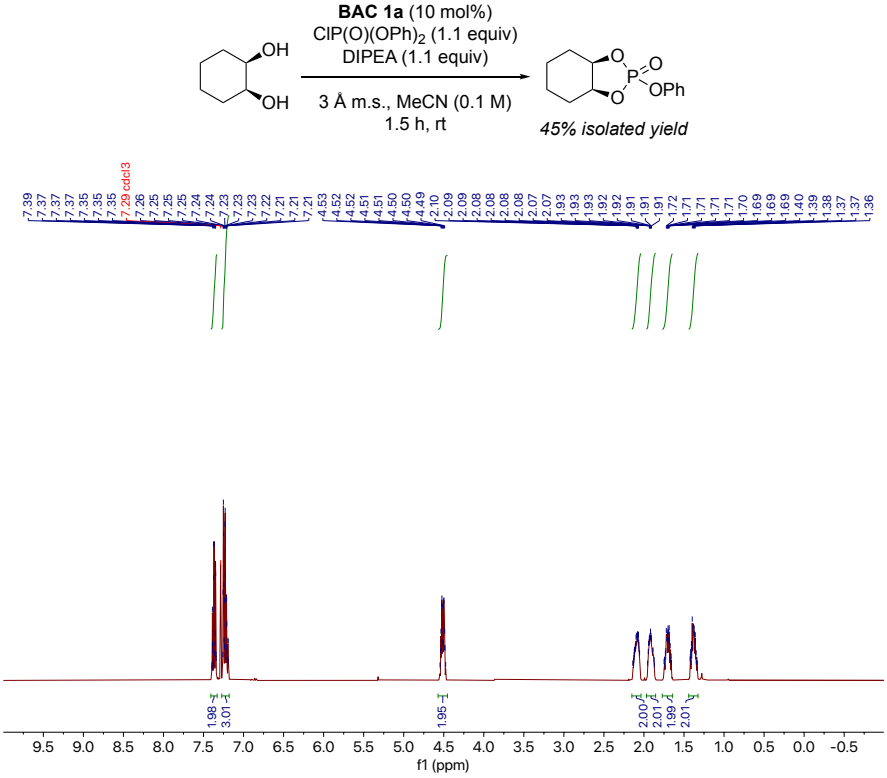
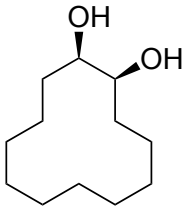


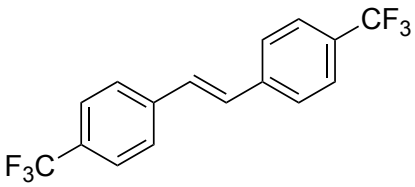
Figure S1: ^{1}H NMR (500 MHz, $CDCl_3$) of isolated cyclized monophosphorylated *cis*-1,2-cyclohexanediol using diphenylchlorophosphate as the phosphorylating agent.

3. Synthesis and Characterization of Monophosphorylated Products

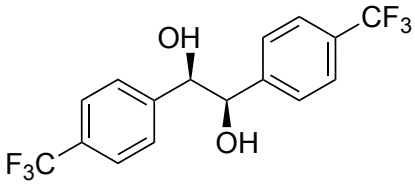
3.1. Synthesis and Characterization of Non-Commercially Available Substrates



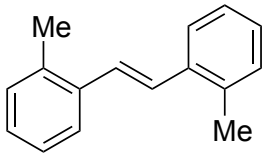
***cis*–1,2-Cyclododecanediol:** Prepared according to a modified literature procedure[6], with cyclododecene (166 mg, 1.00 mmol, 1.00 equiv), AD mix-α (1.5 g, 1.5 g/mmol), *tert*-BuOH (5.0 mL), H_2O (5.0 mL), and methanesulfonamide (95.1 mg, 1.00 mmol, 1.00 equiv). The crude product was purified by column chromatography (70% EtOAc in hexanes), and the product obtained as a white solid (75 mg, 38% yield). A poor yield of *cis*–1,2-diol was obtained due to considerable *cis*/*trans*–diol overlap during purification. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.80 (m, 2H), 1.76 (d, J = 4.9 Hz, 2H), 1.67 (m, 2H), 1.41 (m, 18H).



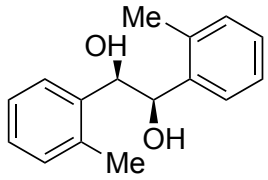
***trans*–1,2-bis(4-Trifluoromethylphenyl)ethene:** Prepared according to a reported literature procedure.[7] In our hands, the reaction required an extended amount of time (18 h) versus the reported reaction time of 2 h.



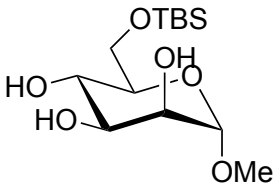
1*R*,2*R*–1,2-(4-Trifluoromethylphenyl)ethane-1,2-diol: Prepared according to a reported literature procedure.[8]



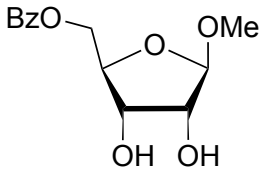
***trans*–1,2-bis(2-Methylphenyl)ethene:** Prepared according to a reported literature procedure.[9]



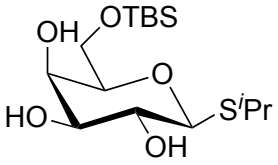
1*R*,2*R*–1,2-(2-Methylphenyl)ethane-1,2-diol: Prepared according to a reported literature procedure.[10]



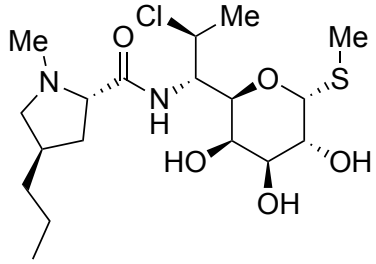
Methyl 6-*O*-(*tert*-Butyldimethylsilyl)-α-D-mannopyranoside: Prepared according to a reported literature procedure.[11]



Methyl 5-*O*-benzoyl β-D-ribofuranoside: Prepared according to a reported literature procedure.[11]



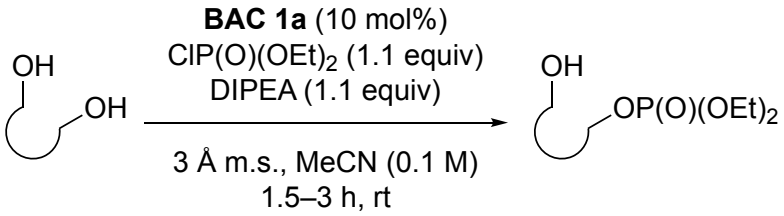
Isopropylthio-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside: Prepared according to a reported literature procedure.[11]



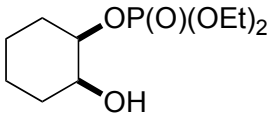
Clindamycin was obtained *via* freebasing of commercially procured clindamycin•HCl with 1 M NaOH washes (3x) in EtOAc.

3.2. Synthesis and Characterization of Monophosphorylated Products

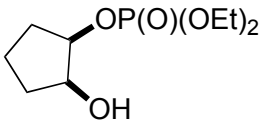
General Procedure for the Monophosphorylation of Diols (**GP1**)



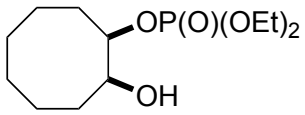
A two-dram vial with a stir bar was charged with diol (1.0 equiv), catalyst **BAC 1a** (10 mol%), 3 Å powdered molecular sieves, DIPEA (1.1 equiv), $ClPO(OEt)_2$ (1.1 equiv) (caution: addition of the electrophile is mildly exothermic), and MeCN (0.1 M). The vial was capped and stirred at room temperature for 1.5–3 hours. Upon completion, the reaction mixture was passed through a pipette cotton filter (to remove molecular sieves) and concentrated *via* rotary evaporation. Purification of the crude material by column chromatography afforded the desired product.



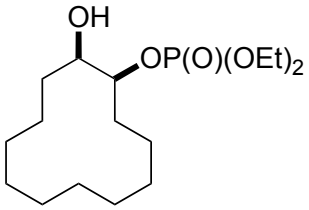
Diethyl (2-hydroxycyclohexyl) phosphate (2a): Prepared according to **GP1** from *cis*–1,2-cyclohexanediol (35 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 1.5 h. Purification by column chromatography (100% EtOAc) afforded the title compound as a colourless oil (75 mg, 99%). When run on a 1.0 mmol scale, a 98% yield was obtained. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.49 (ddd, *J* = 7.3, 7.1, 3.4 Hz, 1H), 4.18–4.06 (m, 4H), 3.84–3.78 (m, 1H), 2.72 (br s, 1H), 2.01–1.90 (m, 1H), 1.80–1.70 (m, 1H), 1.68–1.53 (m, 4H), 1.41–1.26 (m, 8H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 79.3 (d, *J* = 6.1 Hz), 70.0 (d, *J* = 3.9 Hz), 64.1 (d, *J* = 5.8 Hz), 64.0 (d, *J* = 6.0 Hz), 30.1, 29.1 (d, *J* = 4.4 Hz), 21.6, 21.5, 16.2 (d, *J* = 6.8 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.7; **FTIR** (Cast film, cm^{-1}): 3407.07 (br,w), 2983.19 (w), 2938.34 (s), 2864.07 (w), 1725.03 (w), 1448.13 (m), 1394.53(m), 1369.19 (m), 1260.14 (s), 1166.59 (m), 1096.02 (s), 1034.43 (s), 979.23 (s), 818.38 (m); **HRMS** (ESI) for $C_{10}H_{21}NaO_5P$ $[M+Na]^+$: Calculated: 275.1019; Found: 275.1017.



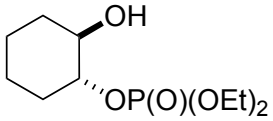
Diethyl (2-hydroxycyclopentyl) phosphate (2b): Prepared according to **GP1** from *cis*–1,2-cyclopentanediol (31 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 1.5 h. Purification by column chromatography (20% acetone in DCM) afforded the title compound as a colourless oil (71 mg, 99%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.58 (dddd, *J* = 5.9, 5.9, 5.9, 4.1 Hz, 1H), 4.21–4.09 (m, 5H), 2.02–1.79 (m, 4H), 1.76–1.63 (m, 1H), 1.62–1.45 (m, 1H), 1.35 (td, *J* = 7.1, 1.0 Hz, 3H), 1.35 (td, *J* = 7.1, 1.0 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 81.3 (d, *J* = 6.2 Hz), 73.5 (d, *J* = 4.0 Hz), 64.3 (d, *J* = 5.8 Hz), 64.2 (d, *J* = 6.0 Hz), 31.4, 30.2, 29.3 (d, *J* = 5.5 Hz), 19.3, 16.3 (d, *J* = 6.8 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.7; **FTIR** (Cast film, cm^{-1}): 3405.37 (br, s), 2975.27 (s), 2913.89 (s), 2876.58 (m), 1731.94 (w), 1649.56 (w), 1478.45 (m), 1444.53 (m), 1394.95 (m), 1369.92 (m), 1343.46 (m), 1257.84 (s), 1166.26 (m), 1100.44 (s), 1036.39 (s); **HRMS** (ESI) for $C_9H_2O_5P$ $[M+H]^+$: Calculated: 239.1043; Found: 239.1044.



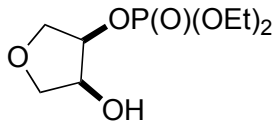
Diethyl (2-hydroxycyclooctyl) phosphate (2c): Prepared according to **GP1** from *cis*–1,2-cyclooctanediol (43 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 1.5 h. Purification by column chromatography (20% acetone in DCM) afforded the title compound as a colourless oil (79 mg, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.62 (dddd, *J* = 9.3, 8.0, 3.4, 2.4 Hz, 1H), 4.13 (m, 4H), 4.02–3.95 (m, 1H), 2.82 (br s, 1H), 2.08 (dddd, *J* = 14.7, 9.0, 9.1, 3.1 Hz, 1H), 1.96–1.45 (m, 11H), 1.35 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 82.4 (d, *J* = 6.4 Hz), 72.2 (d, *J* = 3.9 Hz), 64.14 (d, *J* = 5.8 Hz), 64.07 (d, *J* = 6.0 Hz), 30.3, 30.0 (d, *J* = 4.3 Hz), 26.6, 26.4, 23.4, 22.9, 16.3 (d, *J* = 6.7 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.5; **FTIR** (Cast film, cm^{-1}): 3407.20 (br, s), 2981.58 (s), 2952.79 (s), 2867.23 (s), 1728.28 (w), 1656.54 (w), 1478.60 (m), 1447.65 (m), 1393.96 (m), 1369.14 (m), 1257.37 (s), 1166.16 (m), 1100.43 (m), 1031.29 (br, s); **HRMS** (ESI) for $C_{12}H_{26}O_5P$ $[M+H]^+$: Calculated: 281.1512; Found: 281.1516.



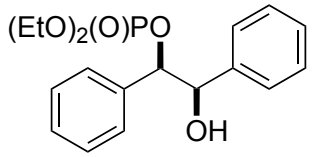
Diethyl (2-hydroxycyclododecyl) phosphate (2d): Prepared according to **GP1** from *cis*–1,2-cyclododecanediol (60 mg, 0.3 mmol, 1 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 1.5 h. Purification by column chromatography (90% EtOAc in Hexanes) afforded the title compound as a colourless oil (68 mg, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.50 (dddd, *J* = 7.8, 7.8, 5.8, 1.4 Hz, 1H), 4.13 (m, 4H), 3.92–3.87 (m, 1H), 3.06 (br s, 1H), 1.80–1.53 (m, 4H), 1.53–1.23 (m, 22H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 82.8, 64.2 (d, *J* = 6.1 Hz), 27.9, 24.8, 23.9, 23.6, 22.0, 21.9, 21.4, 16.32 (d, *J* = 2.3 Hz), 16.27 (d, *J* = 2.4 Hz) ; **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.2, dimerized phosphorylating agent at –13.2; **FTIR** (Cast film, cm^{-1}): 3410.66 (br, m), 2933.25 (s), 2864.90 (m), 1731.94 (w), 1470.53 (m), 1445.82 (m), 1393.45 (m), 1368.91 (w), 1256.86 (m), 1164.92 (m), 1100.91 (m), 1033.51 (s), 1006.19 (s); **HRMS** (ESI) for $C_{16}H_{33}NaO_5P$ $[M+Na]^+$: Calculated: 359.1958; Found: 359.1956.



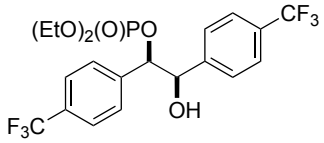
Diethyl (*trans*–2-hydroxycyclohexyl) phosphate (2e): Prepared according to **GP1** from *trans*–1,2-cyclohexanediol (35 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 1.5 h. Purification by column chromatography (100% EtOAc) afforded the title compound as a colourless oil (74 mg, 98%). **^{1}H NMR** (800 MHz, $CDCl_3$): δ 4.18–4.11 (m, 4H), 4.06 (dddd, *J* = 11.6, 8.5, 7.0, 4.9 Hz, 1H), 3.56 (ddd, *J* = 11.0, 8.6, 4.7 Hz, 1H), 2.12–2.08 (m, 1H), 2.07–2.02 (m, 1H), 1.75–1.67 (m, 2H), 1.48–1.41 (m, 1H), 1.36–1.34 (m, 6H), 1.32–1.20 (m, 3H); **^{13}C{^{1}H} NMR** (201 MHz, $CDCl_3$): δ 83.5 (d, *J* = 6.3 Hz), 73.7 (d, *J* = 3.4 Hz), 64.34 (d, *J* = 5.8 Hz), 64.28 (d, *J* = 5.9 Hz), 32.7, 31.9 (d, *J* = 4.5 Hz), 24.2, 23.8, 16.3 (d, *J* = 3.7 Hz), 16.2 (d, *J* = 3.9 Hz); **^{31}P NMR** (324 MHz, $CDCl_3$): δ –0.3 (h, *J* = 7.9, 7.9, 7.9, 7.8, 7.8 Hz) ; **FTIR** (Cast film, cm^{-1}): 3393.97 (br, m), 2983.53 (m), 2937.07 (s), 2863.73 (m), 1726.16 (w), 1452.26 (m), 1394.18 (m), 1258.33 (s), 1083.24 (s), 1028.44 (s), 978.30 (s); **HRMS** (ESI) for $C_{10}H_{21}NaO_5P$ $[M+Na]^+$: Calculated: 275.1019; Found: 275.1017.



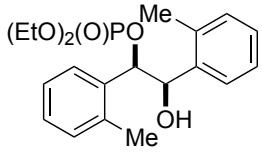
Diethyl (4-hydroxytetrahydrofuran-3-yl) phosphate (2f): Prepared according to **GP1** from 1,4-anhydroerythritol (31 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% Acetone in DCM) afforded the title compound as a colourless oil (42 mg, 58%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.75 (app ddd, *J* = 10.4, 5.6, 4.7 Hz, 1H), 4.39 (ddd, *J* = 5.5, 5.5, 5.5 Hz, 1H), 4.23–4.12 (m, 4H), 4.05 (ddd, *J* = 9.9, 5.5, 1.3 Hz, 1H), 4.02 (dd, *J* = 9.3, 5.9 Hz, 1H), 3.90 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.73 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.14 (br s, 1H), 1.37 (td, *J* = 7.1, 1.0 Hz, 3H), 1.37 (td, *J* = 7.1, 1.0 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 72.3, 71.1 (d, *J* = 3.4 Hz), 70.95, 70.90, 64.8 (d, *J* = 5.9 Hz), 64.6 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 2.2 Hz), 16.2 (d, *J* = 2.2 Hz) ; **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.6, dimerized phosphorylating agent at –13.2; **FTIR** (Cast film, cm^{-1}): 3389.09 (br, m), 2984.20 (m), 2940.28 (m), 2913.20 (m), 2875.97 (m), 1647.31 (w), 1479.95 (m), 1445.02 (m), 1395.34 (m), 1370.75 (w), 1261.53 (s), 1166.24 (m), 1137.91 (s), 1028.76 (s) 983.56 (s); **HRMS** (ESI) for $C_8H_{17}NaO_6P$ $[M+Na]^+$: Calculated: 263.0655; Found: 263.0653.



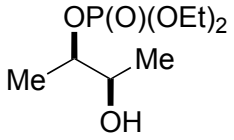
Diethyl (2-hydroxy-1,2-diphenylethyl) phosphate (2g): Prepared according to **GP1** from 1*R*,2*R*–1,2-diphenylethanediol (64 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (80% EtOAc in Hexanes) afforded the title compound as a white solid (84 mg, 80%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.25–7.14 (m, 6H), 7.09–7.06 (m, 4H), 5.27 (dd, *J* = 7.9, 7.9 Hz, 1H), 4.89 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.14–4.04 (m, 1H), 4.03–3.87 (m, 3H), 3.51 (d, *J* = 3.0 Hz, 1H), 1.24 (td, *J* = 7.1, 1.1 Hz, 3H), 1.19 (td, *J* = 7.1, 1.1 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 138.7, 128.6, 128.2 (d, *J* = 7.3 Hz), 128.1, 127.5 (d, *J* = 8.6 Hz), 85.5 (d, *J* = 6.5 Hz), 78.4 (d, *J* = 6.0 Hz), 64.3 (d, *J* = 5.7 Hz), 64.2 (d, *J* = 5.9 Hz), 16.1 (d, *J* = 7.1 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.8; **FTIR** (Cast film, cm^{-1}): 3344.62 (br, m), 3063.89 (w), 3034.13 (w), 2986.19 (m), 2938.22 (w), 2905.80 (w), 1899.10 (w), 1495.88 (w), 1455.62 (m), 1417.13 (w), 1368.13 (w), 1232.71 (m), 1164.82 (m), 1074.54 (s); **HRMS** (ESI) for $C_{18}H_{23}NaO_5P$ $[M+Na]^+$: Calculated: 373.1175; Found: 373.1175.



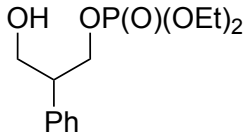
Diethyl (2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethyl) phosphate (2h): Prepared according to **GP1** from 1*R*,2*R*–1,2-(4-trifluoromethylphenyl)ethanediol (105 mg, 0.300 mmol, 1.00 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (10% Acetone in DCM) afforded the title compound as an off-white solid (74 mg, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.38–7.29 (m, 2H), 7.26–7.21 (m, 4H), 5.36 (dd, *J* = 7.6, 7.6 Hz, 1H), 4.98 (d, *J* = 7.1 Hz, 1H), 4.18–3.93 (m, 5H), 1.28 (td, *J* = 7.1, 1.1 Hz, 3H), 1.20 (td, *J* = 7.1, 1.1 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 139.4, 137.4 (d, *J* = 3.6 Hz), 130.6, 128.8, 128.7, 125.6 (d, *J* = 3.7 Hz), 125.1 (d, *J* = 3.9 Hz), 124.2 (d, *J* = 3.9 Hz), 124.1 (d, *J* = 3.8 Hz), 122.8, 83.9 (d, *J* = 5.86 Hz), 77.5 (d, *J* = 5.8 Hz), 64.6 (d, *J* = 5.8 Hz), 64.5 (d, *J* = 5.9 Hz), 16.1 (d, *J* = 6.8 Hz), 16.0 (d, *J* = 6.8 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –1.0; **^{19}F{^{1}H} NMR** (469 MHz, $CDCl_3$): δ –63.0, –62.9; **FTIR** (Cast film, cm^{-1}): 3349.60 (br, m), 3072.30 (w), 2935.59 (m), 1616.95 (w), 1451.47 (m), 1396.07 (m), 1371.21 (m), 1331.43 (s), 1257.17 (s), 1166.46 (s), 1125.35 (s), 1074.52 (s), 1036.76 (s), 911.88 (m); **HRMS** (ESI) for $C_{20}H_{21}F_6NaO_5P$ $[M+Na]^+$: Calculated: 509.0923; Found: 509.0919.



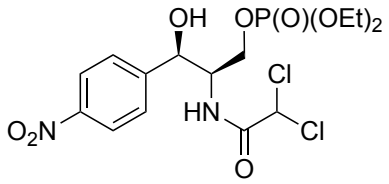
Diethyl (2-hydroxy-1,2-bis(2-(methyl)phenyl)ethyl) phosphate (2i): Prepared according to **GP1** from 1*R*,2*R*–1,2-(2-methylphenyl)ethanediol (73 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (10% Acetone in DCM) afforded the title compound as a colourless oil (84 mg, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.17 (app t, *J* = 7.6 Hz, 2H), 7.14–7.07 (m, 2H), 6.89 (app t, *J* = 8.3 Hz, 2H), 5.58 (dd, *J* = 8.7, 7.6 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 4.14–4.02 (m, 1H), 3.99–3.87 (m, 3H), 3.47 (br s, 1H), 1.76 (s, 3H), 1.73 (s, 3H), 1.24–1.18 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 136.7, 136.2, 135.2 (d, *J* = 2.2 Hz), 130.3 (d, *J* = 4.4 Hz), 128.5, 128.0 (d, *J* = 2.1 Hz), 127.9, 126.0, 125.9, 81.3, 73.9 (d, *J* = 6.7 Hz), 64.2 (d, *J* = 5.6 Hz), 64.0 (d, *J* = 5.7 Hz), 19.0, 18.9, 16.1 (d, *J* = 7.0 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.7; **FTIR** (Cast film, cm^{-1}): 3364.71 (br, s), 3024.73 (m), 2982.35 (s), 2931.27 (m), 2910.12 (m), 1605.30 (w), 1491.66 (m), 1463.40 (m), 1443.48 (m), 1259.07 (s), 1066.65 (s), 1028.97 (s), 757.04 (m); **HRMS** (ESI) for $C_{20}H_{27}NaO_5P$ $[M+Na]^+$: Calculated: 401.1488; Found: 401.1487.



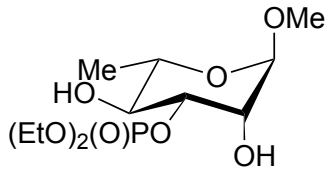
Diethyl (3-hydroxybutan-2-yl) phosphate (2j): Prepared according to **GP1** from 2*R*,3*R*–2,3-butanediol (27 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (100% EtOAc) afforded the title compound as a colourless oil (56 mg, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.29–4.19 (m, 1H), 4.16–4.05 (m, 4H), 3.71 (dq, *J* = 6.4, 6.4 Hz, 1H), 2.79 (br s, 1H), 1.38–1.25 (m, 9H), 1.15 (d, *J* = 6.4 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 80.6 (d, *J* = 6.3 Hz), 70.8 (d, *J* = 5.3 Hz), 64.1 (d, *J* = 5.9 Hz), 64.0 (d, *J* = 5.9 Hz), 18.7, 17.9 (d, *J* = 3.4 Hz), 16.2 (d, *J* = 6.8 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.9; **FTIR** (Cast film, cm^{-1}): 3400.67 (br, m), 2984.20 (m), 2935. 95 (m), 1731.23 (w), 1446.94 (m), 1391.91 (m), 1258.74 (s), 1166.62 (m), 1106.88 (m), 1035.77 (s), 982.53 (m), 819.95 (m); **HRMS** (ESI) for $C_8H_{19}NaO_5P$ $[M+Na]^+$: Calculated: 249.0862; Found: 249.0861.



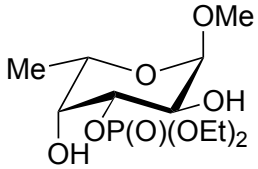
Diethyl (3-hydroxy-2-phenylpropyl) phosphate (2k): Prepared according to **GP1** from 2-phenyl-1,3-propanediol (46 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a colourless oil (54 mg, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.32–7.21 (m, 5H), 4.35–4.29 (m, 2H), 4.10–3.99 (m, 4H), 3.95–3.84 (m, 2H), 3.10 (dddd, *J* = 6.1, 6.1, 6.1, 6.1 Hz, 1H), 2.44 (br s, 1H), 1.33–1.25 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 139.1, 128.8, 128.4, 127.4, 67.8 (d, *J* = 5.9 Hz), 64.2 (d, *J* = 5.9 Hz), 63.1, 48.4 (d, *J* = 5.6 Hz), 16.2 (d, *J* = 6.7 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.1; **FTIR** (Cast film, cm^{-1}): 3401.82 (br, s), 3029.93 (m), 2909.33 (m), 1603.94 (w), 1495.48 (m), 1477.51 (m), 1454.12 (m), 1394. 29 (m), 1256.20 (s), 1165.93 (m), 1021.84 (s); **HRMS** (ESI) for $C_{13}H_{21}NaO_5P$ $[M+Na]^+$: Calculated: 311.1019; Found: 311.1018.



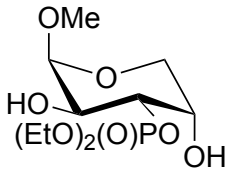
(2*R*,3*R*)-2-(2,2-Dichloroacetamido)-3-hydroxy-3-(4-nitrophenyl)propyl diethyl phosphate (2l): Prepared according to **GP1** from chloramphenicol (97 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (7% MeOH in DCM) afforded the title compound as a brown oil (51 mg, 37%). The product was inseparable from dimer byproduct **3**, present in a 1.83:1 (phosphorylating agent dimer: product) ratio. **^{1}H NMR** (500 MHz, CD_3CN): δ 8.21–8.17 (comp m, AA' portion of AA'BB' spin system, 2H), 7.68–7.62 (comp m, BB' portion of AA'BB' spin system, 2H), 7.31 (d, *J* = 9.4 Hz, 1H), 6.07 (s, 1H), 5.12 (d, *J* = 2.7 Hz, 1H), 4.41–4.31 (comp m, 1H), 4.28–4.15 (m, 2H), 4.13–4.01 (m, 4H, overlap with phosphorylating agent dimer CH_2), 1.37–1.26 (m, 6H, overlap with phosphorylating agent dimer CH_3); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ 165.0, 150.1, 148.5, 128.3, 124.2, 70.9, 67.4, 66.7 (d, *J* = 5.5 Hz), 66.2 (app t, *J* = 3.05 Hz), 65.2 (d, *J* = 2.4 Hz), 65.1 (d, *J* = 2.4 Hz), 56.1 (d, *J* = 7.1 Hz), 16.5 (d, *J* = 6.5 Hz), 16.3 (app t, *J* = 3.5 Hz); **^{31}P{^{1}H} NMR** (202 MHz, CD_3CN): δ –1.1, dimerized phosphorylating agent at –13.4; **FTIR** (Cast film, cm^{-1}): 3253.34 (br, m), 3032.98 (br, m), 2958.34 (m), 2927.02 (s), 2873.20 (m), 1689.66 (s), 1514.96 (m), 1455.05 (m), 1379.66 (m), 1221.38 (s), 1072.65 (s); **HRMS** (ESI) for $C_{15}H_{21}Cl_2N_2NaO_8P$ $[M+Na]^+$: Calculated: 481.0305; Found: 481.0303.



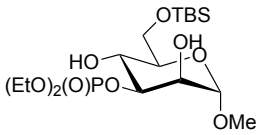
(2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-Dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl diethyl phosphate (2m): Prepared according to **GP1** from methyl α-**L**-rhamnopyranoside (53 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.03 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (40% acetone in DCM) afforded the title compound as a yellow oil (92 mg, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.67 (d, *J* = 1.7 Hz, 1H), 4.40 (ddd, *J* = 8.6, 7.3, 3.3 Hz, 1H), 4.22–4.12 (m, 4H), 4.03 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.83 (br s, 1H), 3.71–3.59 (m, 2H), 3.36 (s, 3H), 2.83 (br s, 1H), 1.40–1.30 (m, 9H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 100.6, 80.1 (d, *J* = 6.0 Hz), 71.6 (d, *J* = 3.3 Hz), 70.2 (d, *J* = 4.6 Hz), 68.1, 64.8 (d, *J* = 5.8 Hz), 55.0, 17.7, 16.23 (d, *J* = 3.0 Hz), 16.18 (d, *J* = 3.1 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.1; **FTIR** (Cast film, cm^{-1}): 3396.67 (br,m), 2983.94 (m), 2935.99 (m), 2915.78 (m), 1447.84 (m), 1393.67 (m), 1250.04 (m), 1133.57 (m), 1059.11 (s), 1027.89 (s), 977.17 (s), 891.23 (m); **HRMS** (ESI) for $C_{11}H_{23}NaO_8P$ $[M+Na]^+$: Calculated: 337.1023; Found: 337.1023.



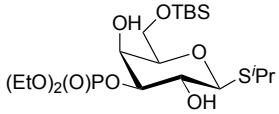
(2*R*,3*S*,4*R*,5*R*,6*S*)-3,5-Dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl diethyl phosphate (2n): Prepared according to **GP1** from methyl α-**L**-fucopyranoside (53 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (50% acetone in DCM) afforded the title compound as a yellow oil (91 mg, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.75 (d, *J* = 3.9 Hz, 1H), 4.44 (ddd, *J* = 10.2, 7.4, 3.1 Hz, 1H), 4.21–4.08 (m, 4H), 3.97 (dd, *J* = 10.1, 4.0 Hz, 1H), 3.95–3.88 (m, 2H), 3.38 (s, 3H), 2.76 (br s, 2H), 1.32 (td, *J* = 7.1, 1.2 Hz, 3H), 1.32 (td, *J* = 7.1, 1.2 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 99.8, 79.1 (d, *J* = 6.0 Hz), 71.3 (d, *J* = 2.7 Hz), 67.6 (d, *J* = 5.4 Hz), 64.5 (d, *J* = 6.0 Hz), 64.3 (d, *J* = 5.9 Hz), 55.5, 16.2 (d, *J* = 3.3 Hz), 16.1 (d, *J* = 1.7 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –1.0; **FTIR** (Cast film, cm^{-1}): 3405.71 (br,m), 2984.54 (m), 2936.61 (m), 2911.10 (m), 2836.01 (w), 1445.34 (m), 1254.59 (m), 1166.54 (m), 1087.24 (s), 1058.97 (s), 1032.76 (s), 961.44 (m), 934.30 (m); **HRMS** (ESI) for $C_{11}H_{23}NaO_8P$ $[M+Na]^+$: Calculated: 337.1023; Found: 337.1021.



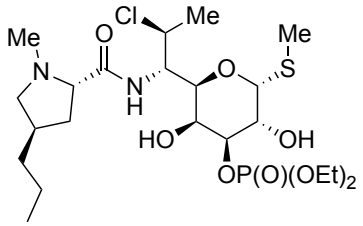
(2*S*,3*R*,4*S*,5*S*)-3,5-Dihydroxy-2-methoxytetrahydro-2H-pyran-4-yl diethyl phosphate (2o): Prepared according to **GP1** from methyl β-**L**-arabinopyranoside (49 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (50% acetone in DCM) afforded the title compound as a colourless oil (74 mg, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.81 (d, *J* = 3.7 Hz, 1H), 4.49 (ddd, *J* = 9.6, 7.4, 3.3 Hz, 1H), 4.24–4.10 (m, 5H), 4.05–3.99 (m, 1H), 3.79 (dd, *J* = 12.6, 1.6 Hz, 1H), 3.72 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.42 (s, 3H), 2.81 (br s, 1H), 2.73 (br s, 1H), 1.37–1.32 (m, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 100.2, 78.3 (d, *J* = 6.0 Hz), 68.6 (d, *J* = 3.1 Hz), 68.1 (d, *J* = 5.2 Hz), 64.6 (d, *J* = 6.0 Hz), 64.4 (d, *J* = 5.9 Hz), 62.1, 55.7, 16.24 (d, *J* = 3.4 Hz), 16.19 (d, *J* = 3.5 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.8; **FTIR** (Cast film, cm^{-1}): 3407.01 (br, m), 2985.10 (m), 2936.51 (m), 2916.87 (m), 1645.95 (w), 1445.70 (m), 1251.72 (s), 1193.55 (m), 1142.96 (m), 1120.86 (m), 1142.96 (m), 1038.99 (s), 1003.36 (s), 903.14 (m); **HRMS** (ESI) for $C_{10}H_{21}NaO_8P$ $[M+Na]^+$: Calculated: 323.0866; Found: 323.0865.



(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-methoxytetrahydro-2H-pyran-4-yl diethyl phosphate (2p): Prepared according to **GP1** from methyl 6-*O*-(tert-butyldimethylsilyl)-α-**D**-galactopyranoside (92 mg, 0.30 mmol, 1.0 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a colourless oil (131 mg, 98%). When run on a 1.0 mmol scale, a 98% yield was obtained. **^{1}H NMR** (800 MHz, $CDCl_3$): δ 4.71 (d, *J* = 1.8 Hz, 1H), 4.44 (ddd, *J* = 9.4, 7.3, 3.3 Hz, 1H), 4.20–4.12 (m, 4H), 4.02 (dd, *J* = 3.5, 1.9 Hz, 1H), 3.94–3.88 (m, 3H), 3.85 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.57 (ddd, *J* = 9.4, 5.4, 4.0 Hz, 1H), 3.35 (s, 3H), 2.82 (br s, 1H), 1.35–1.32 (m, 6H), 0.88 (s, 9H), 0.07 (s, 6H); **^{13}C{^{1}H} NMR** (201 MHz, $CDCl_3$): δ 100.6, 79.9 (d, *J* = 6.0 Hz), 72.2, 69.8 (d, *J* = 4.0 Hz), 67.6 (d, *J* = 4.1 Hz), 64.65 (d, *J* = 5.9 Hz), 64.59 (d, *J* = 5.9 Hz), 63.8, 54.9, 26.0, 18.4, 16.19 (d, *J* = 4.8 Hz), 16.16 (d, *J* = 4.8 Hz), –5.3 (d, *J* = 2.6 Hz); **^{31}P{^{1}H} NMR** (324 MHz, $CDCl_3$): δ –0.3; **FTIR** (Cast film, cm^{-1}): 3387.85 (br, s), 2983.64 (m), 2954.34 (s), 2930.48 (s), 2857.14 (s), 1472.77 (m), 1391.42 (m), 1251.83 (s), 1137.82 (s), 1109.49 (s), 1029.72 (s), 984.03 (s), 911.66 (m), 836.86 (s), 777.46 (m) ; **HRMS** (ESI) for $C_{17}H_{37}O_9PSi$ $[M+H]^+$: Calculated: 445.2017; Found: 445.2015.



(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(((*tert*-Butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-(isopropylthio)tetrahydro-2H-pyran-4-yl diethyl phosphate (2q): Prepared according to **GP1** from isopropylthio-6-*O*-(tert-butyldimethylsilyl)-β-**D**-galactopyranoside (76 mg, 0.30 mmol, 1.00 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a colourless oil (132 mg, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.40 (d, *J* = 9.7 Hz, 1H), 4.28 (ddd, *J* = 9.0, 7.5, 3.2 Hz, 1H), 4.24–4.12 (m, 5H), 3.91–3.80 (m, 3H), 3.50 (dd, *J* = 5.6, 5.6 Hz, 1H), 3.22 (hept, *J* = 6.8 Hz, 1H), 3.15 (br s, 1H), 2.92 (br s, 1H), 1.38–1.30 (m, 12H), 0.88 (s, 9H), 0.07 (d, *J* = 3.3 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 85.8, 81.6 (d, *J* = 5.9 Hz), 77.9, 68.8 (d, *J* = 5.2 Hz), 68.6 (d, *J* = 2.9 Hz), 64.5 (d, *J* = 5.9 Hz), 64.3 (d, *J* = 5.8 Hz), 62.6, 35.3, 25.8, 24.1 (d, *J* = 4.1 Hz), 18.2, 16.1 (d, *J* = 1.5 Hz), 16.0 (d, *J* = 1.4 Hz), –5.5 (d, *J* = 5.1 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –1.0; **FTIR** (Cast film, cm^{-1}): 3390.45 (br, m), 2957.76 (s), 2930.12 (s), 2857.89 (m), 1463.59 (m), 1389.14 (m), 1368.58 (m), 1251.86 (s), 1098.40 (s), 1030.23 (s), 987.05 (m), 914.47 (m), 837.63 (s), 777.23 (m); **HRMS** (ESI) for $C_{19}H_{41}NaO_8PSSi$ $[M+Na]^+$: Calculated: 511.1921; Found: 511.1926.



(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((1*S*)-2-Chloro-1-((4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl diethyl phosphate (2r): Prepared according to **GP1** from clindamycin (128 mg, 0.300 mmol, 1.00 equiv), **BAC 1a** (4.4 mg, 0.030 mmol, 10 mol%), MeCN (3.0 mL), DIPEA (58 µL, 0.33 mmol, 1.1 equiv) and $ClPO(OEt)_2$ (48 µL, 0.33 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a white solid (151 mg, 90%). When run on a 1.0 mmol scale, an 86% yield was obtained. **^{1}H NMR** (500 MHz, CD_3CN): δ 7.93 (d, *J* = 9.3 Hz, 1H), 5.35 (d, *J* = 5.4 Hz, 1H), 4.68 (dddd, *J* = 6.8, 6.8, 6.8, 1.4 Hz, 1H), 4.41 (dd, *J* = 3.9, 0.4 Hz, 1H), 4.29 (dddd, *J* = 10.3, 7.0, 3.3, 0.9 Hz, 1H), 4.23 (ddd, *J* = 10.3, 5.2, 5.2 Hz, 1H), 4.19–4.00 (m, 6H), 3.85 (t, *J* = 3.5 Hz, 1H), 3.70 (d, *J* = 5.0 Hz, 1H), 3.20 (dd, *J* = 8.3, 5.6 Hz, 1H), 3.00 (dd, *J* = 10.6, 4.6 Hz, 1H), 2.39 (s, 3H), 2.18–2.10 (m, 3H), 2.10–2.03 (m, 2H), 1.93–1.79 (m, 2H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.35–1.23 (m, 10H), 0.91–0.87 (m, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ 177.9, 88.6, 78.34 (d, *J* = 5.6 Hz), 70.7, 69.4, 68.4 (d, *J* = 2.6 Hz), 67.5 (d, *J* = 5.7 Hz), 64.9 (d, *J* = 6.0 Hz), 64.7 (d, *J* = 6.0 Hz), 63.4, 59.0, 53.6, 42.2, 38.7, 38.4, 36.5, 23.0, 22.3, 16.5 (d, *J* = 3.0 Hz), 16.4 (d, *J* = 2.9 Hz), 14.6, 13.1; **^{31}P{^{1}H} NMR** (202 MHz, CD_3CN): δ –1.0; **FTIR** (Cast film, cm^{-1}): 3353.87 (br, m), 2962.91 (m), 2928.19 (m), 2872.60 (m), 2789.30 (m), 1657.38 (s), 1511.18 (s), 1454.03 (m), 1263.21 (s), 1102.88 (s), 1069.16 (s), 1035.80 (s), 972.91 (s), 909.23 (m); **HRMS** (ESI) for $C_{22}H_{43}ClN_2O_8PS$ $[M+X]^+$: Calculated: 561.2161; Found: 561.2156.

3.3. Site-Selectivity Assignment Example (2o)

Shown is the process followed for site-selectivity assignments for carbohydrate examples. 2D gCOSY (^{1}H -^{1}H correlation) in conjunction with {^{31}P}^{1}H NMR were employed (broad band decoupling using frequency of ^{31}P NMR peak at –0.8 ppm).

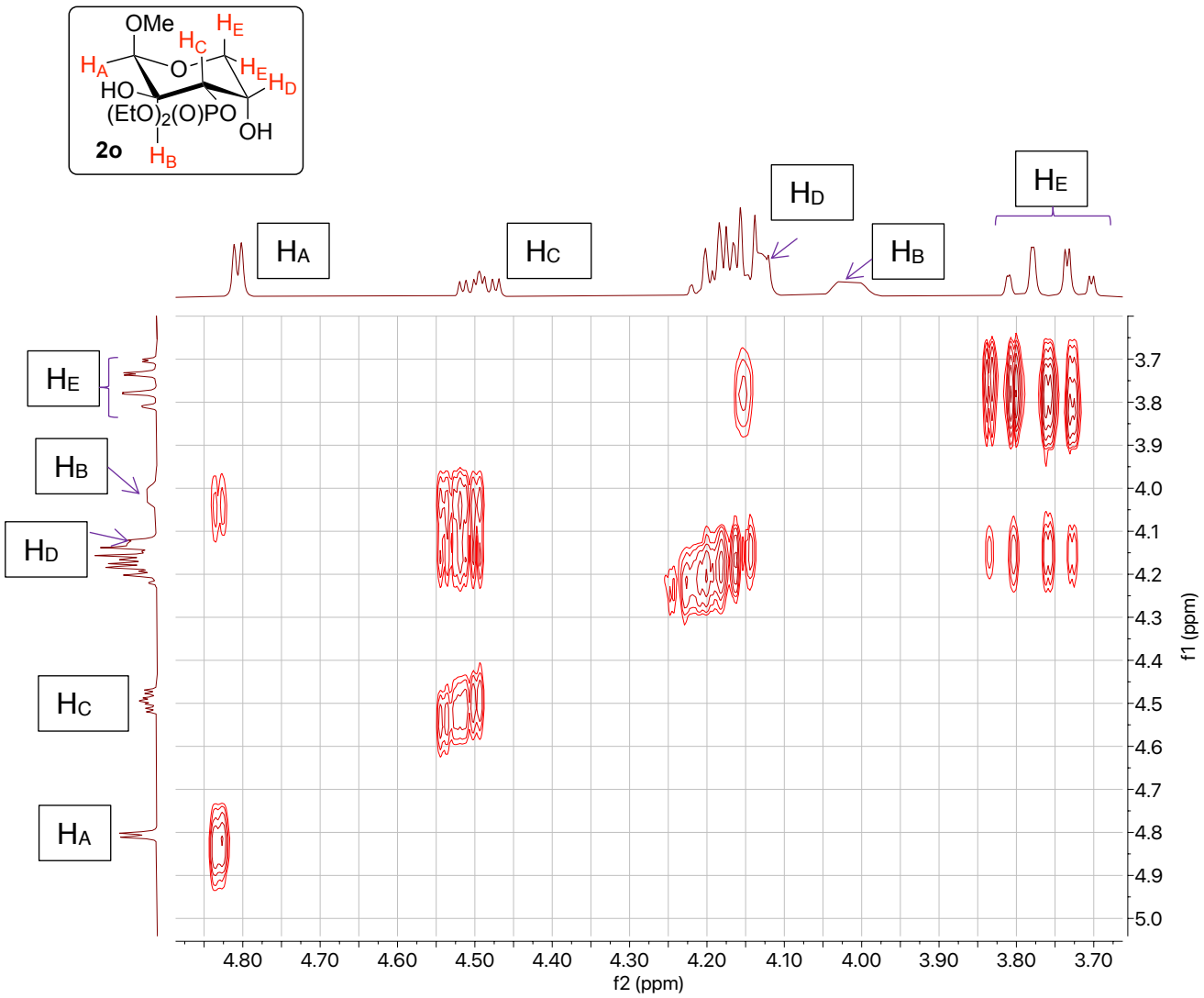


Figure S2: 2D gCOSY (500 MHz, $CDCl_3$) NMR of product **2o**. With the spectrum, proton resonances on the furanose ring were assigned.

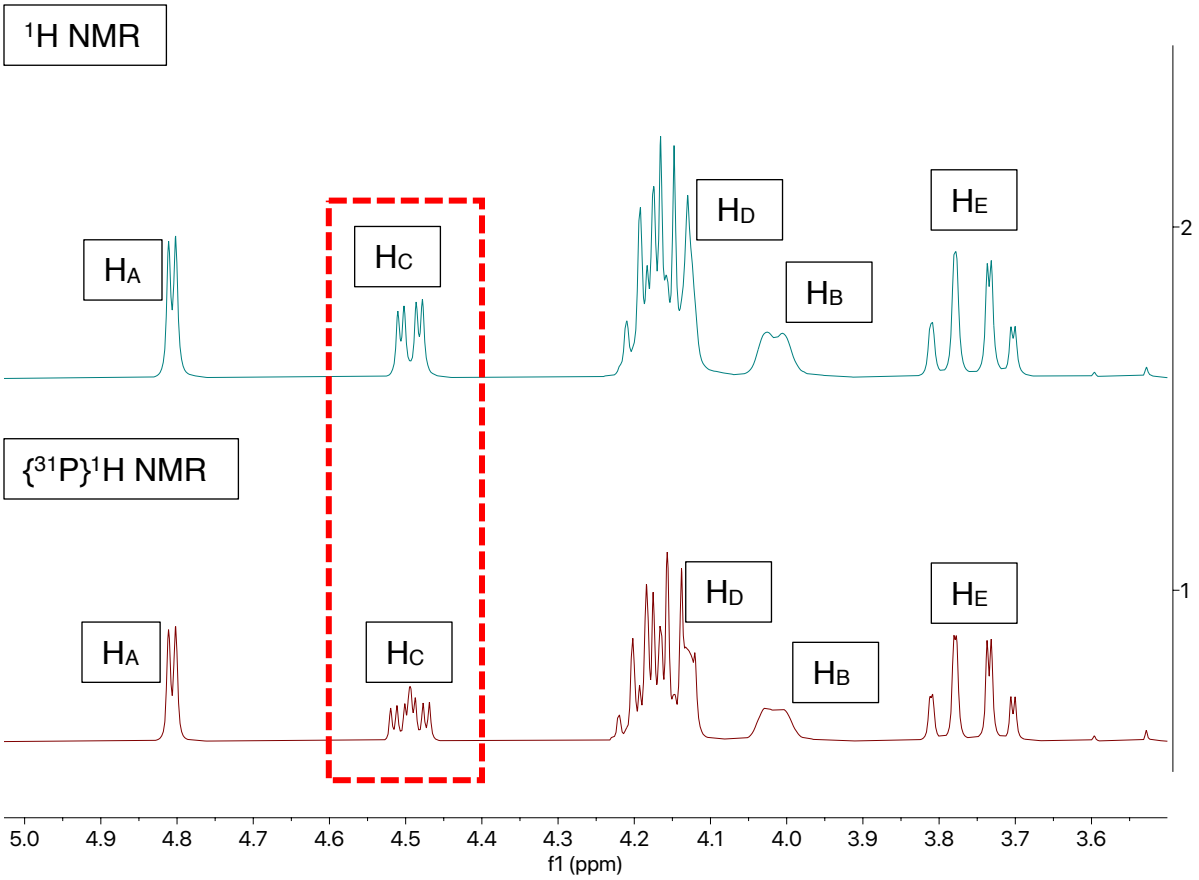
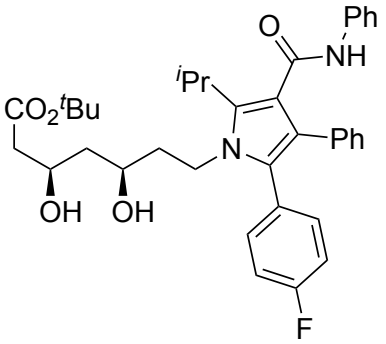


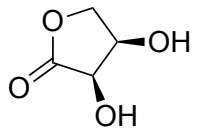
Figure S3: {^{31}P}^{1}H (400 MHz, $CDCl_3$) NMR of product **2o**.

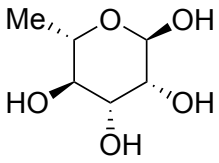
When subjected to ^{31}P decoupled ^{1}H NMR, the proton H_C signal simplifies from a ddd to a dd, losing the 7.4 Hz coupling expected from a ^{3}J ^{31}P–^{1}H, therefore we conclude that the phosphate group was installed at this position.

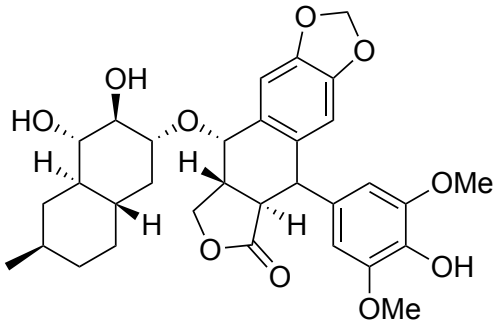
3.4. Scope Limitations

The following substrates did not lead to any observed product formation.









Methyl 5-*O*-benzoyl β-**D**-ribofuranoside led to product formation, but with no site-selectivity (~1:1). Constitutional isomers were isolated as a mixture.

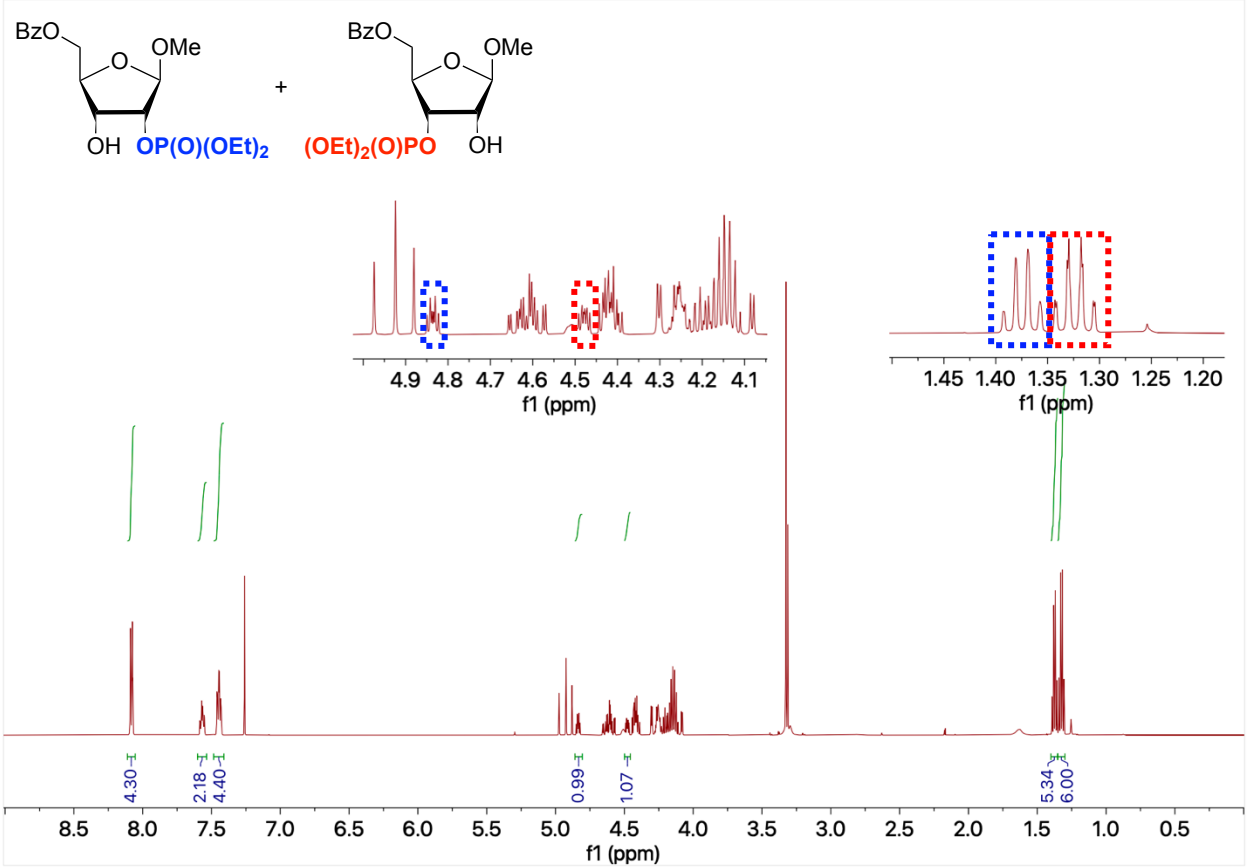
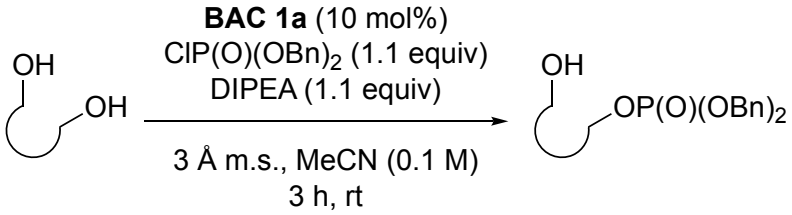


Figure S4: ^{1}H NMR (500 MHz, $CDCl_3$) of isolated product using furanose derivative, with inseparable constitutional isomers highlighted.

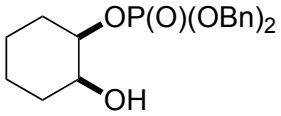
4. Deprotection of Monophosphorylated Products

4.1. Synthesis of Dibenzyl Phosphate Products

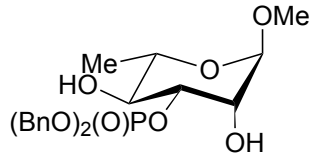
General Procedure for the Monophosphorylation of Diols with Dibenzylchlorophosphate (**GP2**)



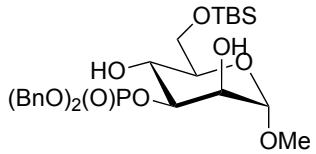
A flame-dried round bottomed flask with a stir bar was charged with diol (1.0 equiv), catalyst **BAC 1a** (10 mol%), 3 Å powdered molecular sieves, DIPEA (1.1 equiv), $ClPO(OBn)_2$ (1.1 equiv) (caution: addition of the electrophile is mildly exothermic), and MeCN (0.1 M). The flask was equipped with a rubber septum and stirred at room temperature for 3 hours. Upon completion, the reaction mixture was passed through a pipette cotton filter (to remove molecular sieves) and concentrated *via* rotary evaporation. Purification by column chromatography afforded the desired product.



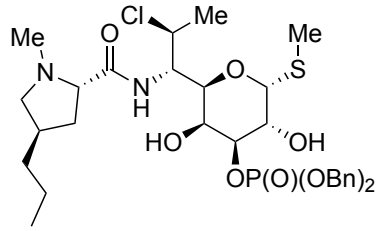
Dibenzyl (2-hydroxycyclohexyl) phosphate (4a): Prepared according to **GP2** from *cis*–1,2-cyclohexanediol (116 mg, 1.00 mmol), **BAC 1a** (14.7 mg, 0.100 mmol, 10 mol%), MeCN (10 mL), DIPEA (0.20 mL, 1.1 mmol, 1.1 equiv), and $ClPO(OBn)_2$ (0.23 mL, 1.1 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (90% EtOAc in Hexanes) afforded the title compound as a white solid (266 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.40–7.30 (m, 10H), 5.13–4.99 (m, 4H), 4.46 (app ddd, *J* = 7.0, 6.5, 3.4 Hz, 1H), 3.78–3.71 (m, 1H), 2.25 (br s, 1H), 1.94–1.83 (m, 1H), 1.74–1.49 (m, 5H), 1.35–1.23 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 135.9 (d, *J* = 2.6 Hz), 135.8 (d, *J* = 2.8 Hz), 128.58 (d, *J* = 1.4 Hz), 128.61, 127.9, 79.7 (d, *J* = 6.2 Hz), 69.7, 69.5 (d, *J* = 5.6 Hz), 69.4 (d, *J* = 5.6 Hz), 28.7, 30.0, 28.7, 21.4, 21.3; **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.8; **FTIR** (Cast film, cm^{-1}): 3405.85 (br, m), 3034.16 (m), 2939.49 (s), 2863.36 (m), 1957.11 (w), 1886.52 (w), 1813.00 (w), 1724.40 (w), 1587.94 (w), 1498.03 (m), 1455.77 (m), 1381.26 (m), 1262.75 (s), 1014.36 (s), 923.57 (m), 884.27 (m), 738.78 (m), 697.04 (m); **HRMS** (ESI) for $C_{20}H_{26}O_5P$ $[M+H]^+$: Calculated: 377.1512; Found: 377.1509.



Dibenzyl ((2R,3R,4R,5S,6S)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl) phosphate (4m): Prepared according to **GP2** from methyl α-**L**-rhamnopyranoside (178 mg, 1.00 mmol), **BAC 1a** (14.7 mg, 0.100 mmol, 10.0 mol%), MeCN (10 mL), DIPEA (0.20 mL, 1.1 mmol, 1.1 equiv), and $ClPO(OBn)_2$ (0.23 mL, 1.1 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a white solid (197 mg, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.41–7.30 (m, 10H), 5.15–5.02 (m, 4H), 4.62 (dd, *J* = 1.8, 0.9 Hz, 1H), 4.39 (ddd, *J* = 7.1, 5.2, 3.3 Hz, 1H), 3.86 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.67–3.55 (m, 2H), 3.34 (s, 3H), 1.36–1.31 (m, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 135.5, 129.0, 128.9 (d, *J* = 2.9 Hz), 128.3 (d, *J* = 5.9 Hz), 100.3, 80.7 (d, *J* = 5.9 Hz), 71.7 (d, *J* = 3.0 Hz), 70.4 (d, *J* = 5.7 Hz), 70.4 (d, *J* = 5.8 Hz), 70.15 (d, *J* = 5.1 Hz), 68.0, 17.7; **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.8; **FTIR** (Cast film, cm^{-1}): 3391.10 (br, m), 3034.27 (m), 2936.27 (m), 2908.46 (m), 2833.24 (w), 1963.75 (w), 1815.13 (w), 1708.61 (w), 1588.22 (w), 1498.21 (m), 1456.06 (m), 1384.06 (m), 1328.97 (w), 1256.26 (s), 1131.28 (s), 1058.98 (s), 1019.82 (s), 897.37 (m), 739.14 (m), 697.52 (m); **HRMS** (ESI) for $C_{21}H_{28}O_8P$ $[M+H]^+$: Calculated: 439.1516; Found: 439.1513.



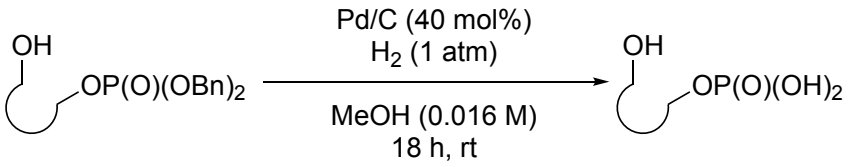
Dibenzyl ((2*R*,3*R*,4*S*,5*S*,6*S*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-methoxytetrahydro-2H-pyran-4-yl) phosphate (4p): Prepared according to **GP1** from methyl 6-*O*-(*tert*-butyldimethylsilyl)-α-**D**-galactopyranoside (308 mg, 1.00 mmol), **BAC 1a** (14.7 mg, 0.100 mmol, 1.00 mol%), MeCN (10 mL), DIPEA (0.20 mL, 1.1 mmol, 1.1 equiv) and $ClPO(OBn)_2$ (0.23 mL, 1.1 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (30% acetone in DCM) afforded the title compound as a colourless oil (377 mg, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39–7.29 (m, 10H), 5.12–5.00 (m, 4H), 4.66 (d, *J* = 1.7 Hz, 1H), 4.53 (ddd, *J* = 7.9, 3.1, 1.8 Hz, 1H), 3.88 (ddd, *J* = 9.5, 3.1, 2.0 Hz, 1H), 3.85 (d, *J* = 5.0 Hz, 2H), 3.68 (t, *J* = 9.5 Hz, 1H), 3.56 (ddd, *J* = 9.7, 5.0, 5.0 Hz, 1H), 3.31 (s, 3H), 0.90 (s, 9H), 0.09 (s, 6H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ 135.8 (d, *J* = 5.0 Hz), 135.7 (d, *J* = 4.5 Hz), 128.8–128.7 (m), 128.2 (d, *J* = 7.3 Hz), 99.2 (d, *J* = 5.3 Hz), 76.5 (d, *J* = 5.5 Hz), 71.8, 70.6 (d, *J* = 3.7 Hz), 70.0 (d, *J* = 5.8 Hz), 69.9 (d, *J* = 5.7 Hz), 69.8, 64.3, 55.0, 26.0, 18.4, –5.27 (d, *J* = 4.0 Hz); **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$): δ –0.6; **FTIR** (Cast film, cm^{-1}): 3388.80 (br, m), 3035.50 (w), 2953,83 (m), 2929.41 (m), 2856.57 (m), 1498.28 (w), 1456.73 (m), 1253.40 (s), 111.27 (s), 1021.19 (s), 837.63 (m), 779.09 (m), 739.40 (m), 697.04 (m), 673.32 (w); **HRMS** (ESI) for $C_{27}H_{41}NaO_9PSi$ $[M+Na]^+$: Calculated: 591.2150; Found: 591.2155.



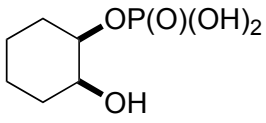
Dibenzyl ((2*R*,3*S*,4*S*,5*R*,6*R*)-2-((1*R*,2*S*)-2-chloro-1-((2*R*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl) phosphate (4r): Prepared according to **GP2** from clindamycin (425 mg, 1.00 mmol), **BAC 1a** (14.7 mg, 0.100 mmol, 10.0 mol%), MeCN (10 mL), DIPEA (0.20 mL, 1.10 mmol, 1.10 equiv), and $ClPO(OBn)_2$ (0.23 mL, 1.1 mmol, 1.1 equiv) for 3 h. Purification by column chromatography (40% acetone in DCM) afforded the title compound as a colourless oil (206 mg, 30%). **^{1}H NMR** (500 MHz, CD_3CN): δ 7.96 (d, *J* = 9.6 Hz, 1H), 7.43–7.31 (m, 10H), 5.38 (d, *J* = 5.5 Hz, 1H), 5.12–5.00 (m, 4H), 4.68 (qd, *J* = 6.7, 1.4 Hz, 1H), 4.52 (d, *J* = 3.9 Hz, 1H), 4.40 (ddd, *J* = 10.4, 7.1, 3.2 Hz, 1H), 4.32 (ddd, *J* = 10.3, 5.2, 5.2 Hz, 1H), 4.19 (ddd, *J* = 9.8, 9.7, 1.5 Hz, 1H), 4.11 (d, *J* = 10.0 Hz, 1H), 3.95 (t, *J* = 3.5 Hz, 1H), 3.84 (d, *J* = 5.2 Hz, 1H), 3.22–3.13 (m, 1H), 2.98 (dd, *J* = 10.8, 4.6 Hz, 1H), 2.38 (s, 3H), 2.15–2.06 (m, 4H), 2.02 (dd, *J* = 10.4, 8.5 Hz, 1H), 1.87 (ddd, *J* = 12.7, 7.6, 4.0 Hz, 1H), 1.73 (ddd, *J* = 13.0, 10.8, 9.7 Hz, 1H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.26–1.10 (m, 4H), 0.81–0.77 (m, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN): δ 177.9, 137.3 (d, *J* = 7.0 Hz), 137.2 (d, *J* = 7.3 Hz), 129.5 (d, *J* = 4.9 Hz), 129.4 (d, *J* = 7.2 Hz), 128.93 (d, *J* = 9.6 Hz), 88.6, 78.9 (d, *J* = 5.8 Hz), 70.2 (d, *J* = 5.7 Hz), 70.0 (d, *J* = 5.6 Hz), 69.4, 68.5 (d, *J* = 2.4 Hz), 67.4 (d, *J* = 6.1 Hz), 63.4, 59.1, 53.6, 42.3, 38.7, 38.4, 36.5, 23.1, 22.2, 14.6, 13.1; **^{31}P{^{1}H} NMR** (202 MHz, CD_3CN): δ –1.4 (s); **FTIR** (Cast film, cm^{-1}): 3346.20 (br, m), 3034.43 (w), 2956.35 (m), 2926.99 (m), 2872.46 (m), 2790.88 (m), 1656.74 (s), 1511.24 (s), 1455.77 (m), 1380.69 (m), 1265.39 (s), 1216.16 (m), 1077.18 (s), 1016.73 (s), 972.13 (m), 919.92 (m), 737.38 (m), 697.58 (s); **HRMS** (ESI) for $C_{32}H_{47}ClN_2O_8PS$ $[M+H]^+$: Calculated: 685.2474; Found: 685.2473.

4.2. Deprotection of Dibenzyl Phosphate Products

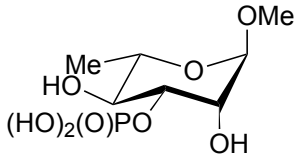
General Procedure for the Deprotection of Dibenzyl Phosphate Products (**GP3**)



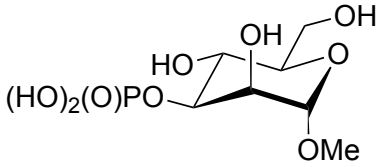
Following a modified literature procedure,[12] a flame-dried round bottomed flask equipped with a stir bar was charged with Pd/C (40 mol%), and dibenzyl phosphate product (1.0 equiv). The flask was evacuated and filled with hydrogen three times and allowed to stir at room temperature for 18 hours, under a balloon of hydrogen. Upon completion, the reaction mixture was passed through a celite pad, and concentrated *via* rotary evaporation, yielding the deprotected phosphate product.



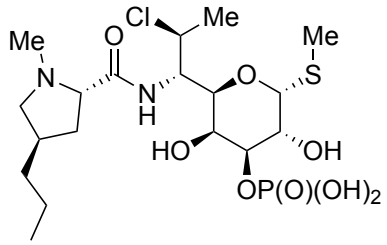
2-Hydroxycyclohexyl dihydrogen phosphate (5a): Prepared according to **GP3** from dibenzyl (2-hydroxycyclohexyl) phosphate (113 mg, 0.300 mmol), Pd/C (12.8 mg, 0.120 mmol), and MeOH (19 mL) for 18 h. Compound isolated as a white solid (58 mg, 99%). **^{1}H NMR** (500 MHz, CD_3OD): δ 4.34 (app dd, *J* = 7.2, 7.2 Hz, 1H), 3.85–3.79 (m, 1H), 1.98 (dd, *J* = 9.2, 8.6 Hz, 1H), 1.82–1.72 (m, 1H), 1.71–1.54 (m, 4H), 1.42–1.28 (m, 2H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3OD): δ 78.6, 70.1, 31.0, 29.7, 22.5; **^{31}P{^{1}H} NMR** (202 MHz, CD_3OD): δ –0.0; **FTIR** (Cast film, cm^{-1}): 3307.88 (br, m), 2939.41 (s), 2861.84 (s), 1721.21 (br, m), 1450.49 (m), 1194.63 (m), 1143.81 (m), 1021.56 (s), 975.28 (m); **HRMS** (ESI) for $C_6H_{13}O_5P$ $[M–X]^-$: Calculated: 195.0428; Found: 195.0427.



(2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-Dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl dihydrogen phosphate (5m): Prepared according to **GP3** from dibenzyl ((2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl) phosphate (132 mg, 0.300 mmol), Pd/C (12.8 mg, 0.120 mmol), and MeOH (19 mL) for 18 h. Compound isolated as a light brown solid (77 mg, 99%). **^{1}H NMR** (500 MHz, CD_3OD): δ 4.58 (d, *J* = 1.6 Hz, 1H), 4.30 (ddd, *J* = 8.7, 8.5, 3.1 Hz, 1H), 4.07–4.02 (m, 1H), 3.65–3.52 (m, 1H), 3.36 (s, 3H), 1.29 (d, *J* = 5.7 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3OD): δ 102.5, 101.1, 78.7 (d, *J* = 5.6 Hz), 72.5 (d, *J* = 4.6 Hz), 71.0, 70.0, 55.1, 18.1; **^{31}P{^{1}H} NMR** (202 MHz, CD_3OD): δ –0.2; **FTIR** (Cast film, cm^{-1}): 3359.79 (br, s), 2935.98 (br, s), 2839.28 (s), 1698.15 (m), 1451.89 (m), 1386.39 (m), 1199.74 (s), 1129.17 (s), 1054.54 (s), 977.11 (s), 866.31(m), 789.54 (m), 736.54 (m), 702.85 (w), 661.36 (m); **HRMS** (ESI) for $C_7H_{15}O_8P$ [M–X]$^-$: Calculated: 257.0432; Found: 257.0430.



(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2H-pyran-4-yl dihydrogen phosphate (5p): Prepared according to **GP3** from dibenzyl ((2*R*,3*R*,4*S*,5*S*,6*S*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-methoxytetrahydro-2H-pyran-4-yl) phosphate (171 mg, 0.300 mmol), Pd/C (12.8 mg, 0.120 mmol), and MeOH (19 mL) for 18 h. Compound isolated as a white solid (81 mg, 99%). **^{1}H NMR** (500 MHz, CD_3OD): δ 4.66 (d, *J* = 1.8 Hz, 1H), 4.36 (ddd, *J* = 9.4, 8.2, 3.3 Hz, 1H), 4.05 (dd, *J* = 3.3, 1.8 Hz,1H), 3.88–3.76 (m, 2H), 3.73 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.55 (ddd, *J* = 9.8, 5.6, 2.3 Hz, 1H), 3.39 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3OD): δ 102.5, 79.1 (d, *J* = 5.3 Hz), 74.4, 70.8, 67.1, 62.7, 55.2, 49.8; **^{31}P{^{1}H} NMR** (202 MHz, CD_3OD): δ –0.1; **FTIR** (Cast film, cm^{-1}): 3347.66 (br, m), 2947.07 (br, m), 2842.26 (m), 2285.19 (br, w), 1685 (br, w), 1448.92 (m), 1199.50 (m), 1133.54 (s), 1106.04 (s), 1059.78 (s), 980.47 (s); **HRMS** (ESI) for $C_7H_{14}O_9P$ [M–X]$^-$: Calculated: 273.0381; Found: 273.0382.

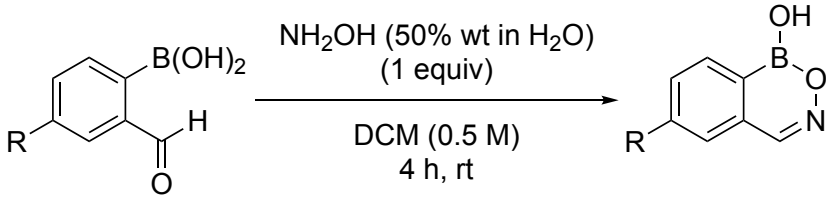


(2*R*,3*S*,4*S*,5*R*,6*R*)-2-((1*R*,2*S*)-2-Chloro-1-((2*R*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl dihydrogen phosphate (5r): Prepared according to **GP3** from dibenzyl ((2*R*,3*S*,4*S*,5*R*,6*R*)-2-((1*R*,2*S*)-2-chloro-1-((2*R*,4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl) phosphate (206 mg, 0.300 mmol), Pd/C (12.8 mg, 0.120 mmol), and MeOH (3 mL) for 18 h. Compound isolated as a colourless residue (141 mg, 99%). **^{1}H NMR** (500 MHz, CD_3OD): δ 5.38 (d, *J* = 5.5 Hz, 1H), 4.68–4.60 (m, 1H), 4.58 (dd, *J* = 7.0, 6.5 Hz, 1H), 4.39 (d, *J* = 9.9 Hz, 1H), 4.34–4.22 (m, 3H), 4.15 (br s, 1H), 3.81 (dd, *J* = 11.0, 6.7 Hz, 1H), 3.37 (s, 3H), 3.01–2.91 (m, 4H), 2.46–2.21 (m, 4H), 2.19 (s, 3H), 1.53 (dd, *J* = 7.4, 7.0 Hz, 2H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.45–1.29 (m, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3OD): δ 170.3, 90.4, 78.8, 71.1, 70.4, 69.3, 63.1, 60.0, 55.4, 50.8, 42.3, 38.9, 37.7, 36.7, 24.0, 23.0, 15.1, 14.3; **^{31}P{^{1}H} NMR** (202 MHz, CD_3OD): δ –0.1; **FTIR** (Cast film, cm^{-1}): 3349.93 (br, s), 3051.51 (br, m), 2958.71 (s), 2928.16 (s), 1686.95 (s), 1553.49 (m), 1454.42 (m), 1380.28 (m), 1319.59 (m), 1257.17 (m), 1151.27 (m), 1073.11 (s), 990.49 (s), 962.14 (s); **HRMS** (ESI) for $C_{18}H_{33}ClN_2O_8P$ $[M–X]^-$: Calculated: 503.1389; Found: 503.1381.

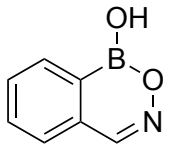
5. Synthesis and Characterization of Benzoxazaborine Variants

5.1. Synthesis of Benzoxazaborine Catalysts

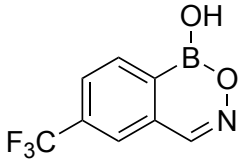
General Procedure for the Synthesis of Benzoxazaborine Catalysts (**GP4**)[1]



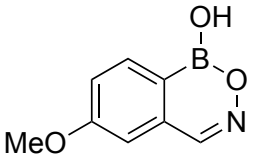
In a round bottom flask equipped with a stir bar under air, 2-formylphenylboronic acid (1.0 equiv) was dissolved in DCM (0.5 M) and stirred for 10 minutes, after which NH_2OH (50% wt in H_2O, 1.0 equiv) was added in one portion. The mixture was stirred at room temperature for 4 hours, during which a precipitate formed. Upon completion, the precipitate was collected by vacuum filtration, washed with H_2O (6 x 20 mL), and dried under vacuum filtration to afford the title compound as a solid.



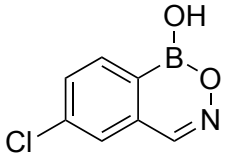
1H-Benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1a): Prepared according to **GP4** from 2-formylphenylboronic acid (840 mg, 5.0 mmol), NH_2OH (50% wt. in H_2O) (0.31 mL, 5.0 mmol), and MeOH (10 mL) for 4 h. Compound isolated as a white solid (660 mg, 91%). The collected spectra are in agreement with data from a previously reported synthesis.[1]



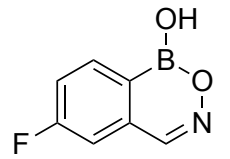
6-(Trifluoromethyl)-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1b): Prepared according to **GP4** from (2-formyl-4-(trifluoromethyl)phenyl)boronic acid (1.1 g, 5.0 mmol), NH_2OH (50% wt. in H_2O) (0.31 mL, 5.0 mmol), and MeOH (10 mL) for 4 h. Compound isolated as a white solid (645 mg, 60%). **^{1}H NMR** (500 MHz, acetone-d_6, drop D_2O): δ 9.26 (br s, 1H), 8.72 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 8.15 (s, 1H), 8.06 (d, J = 7.9 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6, drop D_2O): δ150.3, 134.3, 134.0, 128.7 (d, J = 3.7 Hz), 125.07 (d, J = 4.1 Hz), 126.0, 123.8; **^{11}B{^{1}H} NMR** (160 MHz, acetone-d_6, drop D_2O): δ 28.1; **^{19}F{^{1}H} NMR** (470 MHz, acetone-d_6, drop D_2O): δ –63.7; **FTIR** (Cast film, cm^{-1}): 3430.52 (br, m), 3183.12 (br,m) 2952.00 (br, w), 2683.07 (br, m), 1405.48 (m), 1342.44 (s), 1146.27 (s), 1073.93 (s), 1032.55 (s), 919.89 (s), 896.45 (m); **HRMS** (ESI) for $C_8H_6[^{11}B]F_3NO_2$ $[M+H]^+$: Calculated: 216.0440; Found: 216.0440.



6-Methoxy-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1c): Prepared according to **GP4** from (2-formyl-4-(methoxy)phenyl)boronic acid (900 mg, 5 mmol), NH_2OH (50% wt. in H_2O) (0.31 mL, 5.0 mmol), and MeOH (10 mL) for 4 h. Compound isolated as a white solid (672 mg, 76%). **^{1}H NMR** (500 MHz, CD_3CN, drop D_2O): δ 8.39 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.56 (br s, 1H), 3.90 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, CD_3CN, drop D_2O): δ 164.4, 151.2, 135.8, 135.5, 120.6, 111.4, 56.3; **^{11}B{^{1}H} NMR** (160 MHz, CD_3CN, drop D_2O): δ 28.5; **FTIR** (Cast film, cm^{-1}): 3201.48 (br, m), 2984.36 (w), 2851.71 (w), 1619.26 (m), 1596.45 (m), 1560.13 (m), 1402.09 (s), 1345.56 (m), 1238.11 (m), 1173.74 (m), 1052.62 (m), 909.61 (m); **HRMS** (ESI) for $C_8H_9[^{11}B]NO_3$ $[M+H]^+$: Calculated: 178.0670; Found: 178.0668.



6-Chloro-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1d): Prepared according to **GP4** from (2-formyl-4-(chloro)phenyl)boronic acid (920 mg, 5.0 mmol), NH_2OH (50% wt. in H_2O) (0.31 mL, 5.0 mmol), and MeOH (10 mL) for 4 h. Compound isolated as a white solid (624 mg, 69%). **^{1}H NMR** (500 MHz, acetone-d_6, drop D_2O): δ 8.56 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 2.0 Hz, 1H); **^{13}C{^{1}H} NMR** (126 MHz, acetone-d_6, drop D_2O): δ 149.6, 139.1, 135.1, 134.4, 132.5, 127.4; **^{11}B{^{1}H} NMR** (160 MHz, acetone-d_6, drop D_2O): δ 28.2; **FTIR** (Cast film, cm^{-1}): 3052.84 (br, m), 1611.82 (m), 1587.52 (m), 1547.91 (m), 1438.97 (m), 1412.52 (m), 1396.15 (s), 1325.35 (m), 1293.15 (m), 1241.88 (m), 1090.30 (m), 1049.60 (m), 925.85 (m), 903.87 (m), 833.07 (m); **HRMS** (ESI) for $C_7H_6[^{11}B]ClNO_2$ $[M+H]^+$: Calculated: 182.0175; Found: 182.0179.



6-Fluoro-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1e): Prepared according to **GP4** from (2-formyl-4-(fluoro)phenyl)boronic acid (840 mg, 5.0 mmol), NH_2OH (50% wt. in H_2O) (0.31 mL, 5.0 mmol), and MeOH (10 mL) for 4 h. Compound isolated as a white solid (693 mg, 84%). The collected spectra are in agreement with data from a previously reported synthesis.[13]

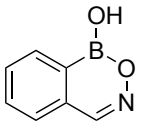
5.2. pK_a Determination of Benzoxazaborine Variants

General Procedure for the Determination of Boron Heterocycle pK_a in MeCN/H_2O by ^{11}B NMR (GP5)

pK_a value for **BAC 1a** was determined in a previous publication, but reproduced below.[1] **BAC 1b**, **BAC 1c**, **BAC 1d**, **BAC 1e** (0.50 mmol) was dissolved in 25 mL MeCN. The solution was further diluted with 25 mL of a phosphate buffer solution which was prepared by dissolving 1.4 g potassium phosphate monobasic monohydrate in 80 mL deionized water, and 20 mL D_2O (the final sample is 10% D_2O). From the resulting boron heterocycle stock solution, 4.5 mL aliquots were transferred to 3-dram vials. The pH of the solution of these aliquots was then adjusted using 1.0 M HCl, 1.0 M NaOH and measured using a pH meter. After the pH was adjusted, approximately 700 μL of each aliquot was transferred to an NMR tube and analyzed by ^{11}B NMR spectroscopy, using D_2O as the solvent for locking and shimming.

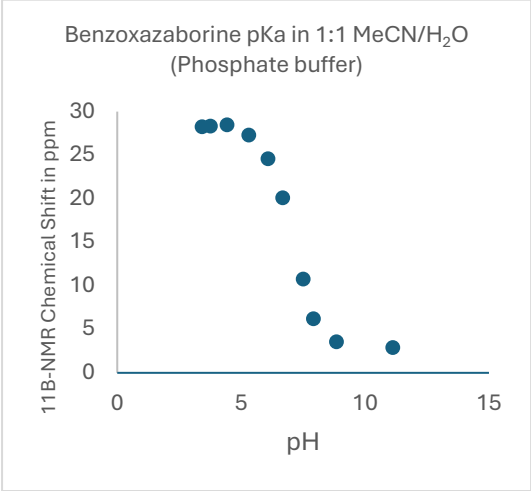
5.2.1. Calculations to Determine pK_a Values

The chemical shift observed by ^{11}B NMR was plotted as a function of the solution pH. To calculate the pK_a, a plot was constructed of pH as a function of $log\frac{(\delta_{highest})-(\delta_{pH})}{(\delta_{pH})-(\delta_{lowest})}$ where $(\delta_{highest})$ is the most downfield chemical shift observed by ^{11}B NMR spectroscopy during the titration (observed at the most acidic pH where the equilibrium is entirely towards the free acid), (δ_{lowest}) is the most upfield chemical shift observed by ^{11}B NMR spectroscopy during the titration (observed at the most downfield alkaline pH where the equilibrium is entirely towards the conjugate base), and δ_{pH} is the observed chemical shift by ^{11}B NMR spectroscopy at a particular pH. The pK_a is determined by the y-intercept of this plot.[1]



1a
pK_a 7.02

Following **GP5**, the pK_a of **BAC 1a** in 1:1 MeCN/H_2O was calculated to be 7.02.



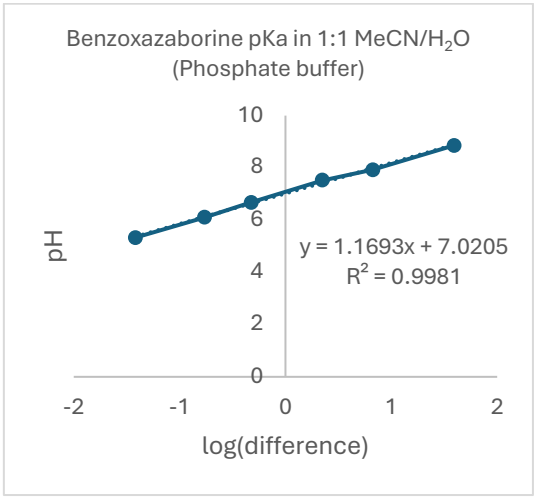
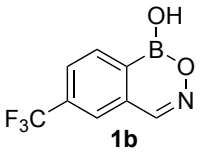
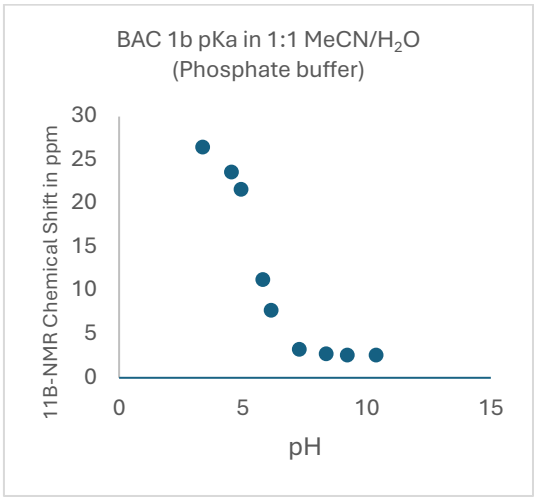


Figure S5: pK_a determination of **BAC 1a** in 1:1 MeCN/H_2O.



1b
pK_a 5.54

Following **GP5**, the pK_a of **BAC 1b** in 1:1 MeCN/H_2O was calculated to be 5.54.



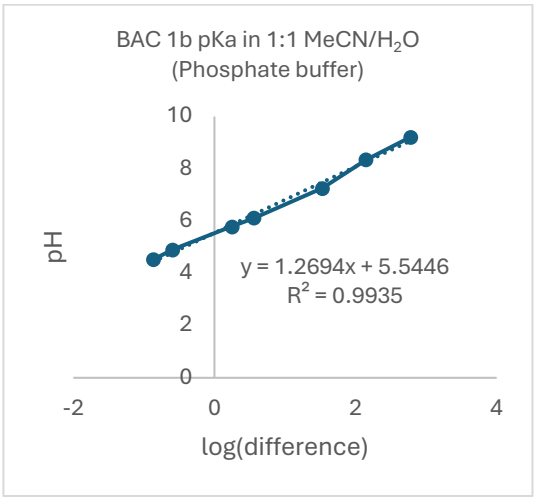
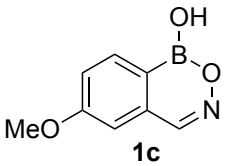


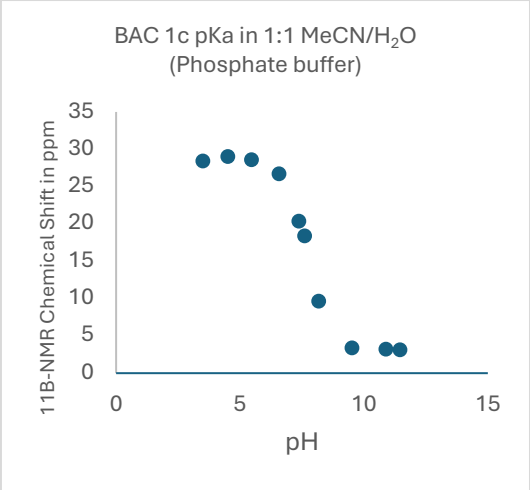
Figure S6: pK_a determination of **BAC 1b** in 1:1 MeCN/H_2O.



1c

pK_a 7.69

Following **GP5**, the pK_a of **BAC 1c** in 1:1 MeCN/H_2O was calculated to be 7.69.



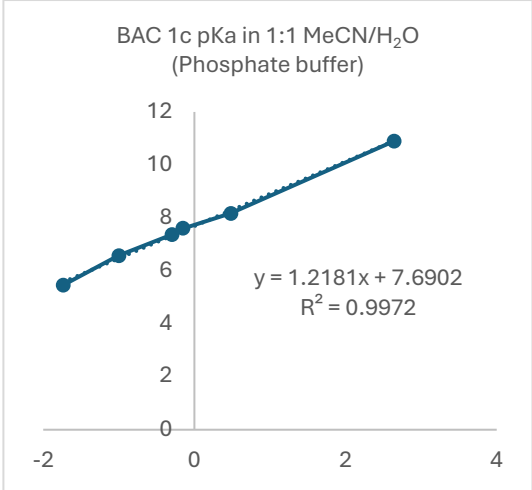
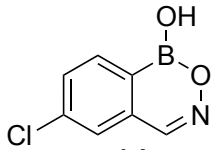


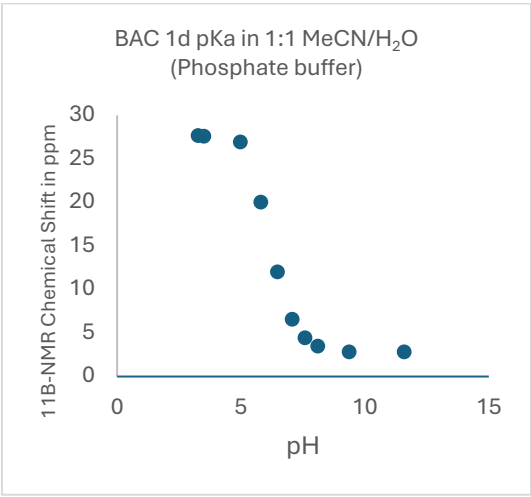
Figure S7: pK_a determination of **BAC 1c** in 1:1 MeCN/H_2O.



1d

pK_a 6.24

Following **GP5**, the pK_a of **BAC 1d** in 1:1 MeCN/H_2O was calculated to be 6.24.



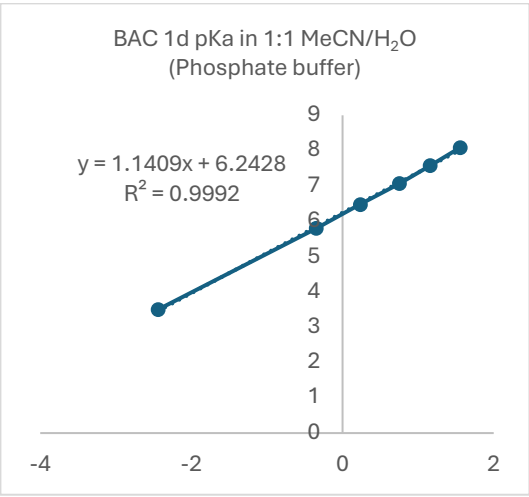
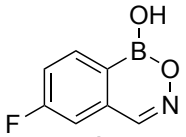
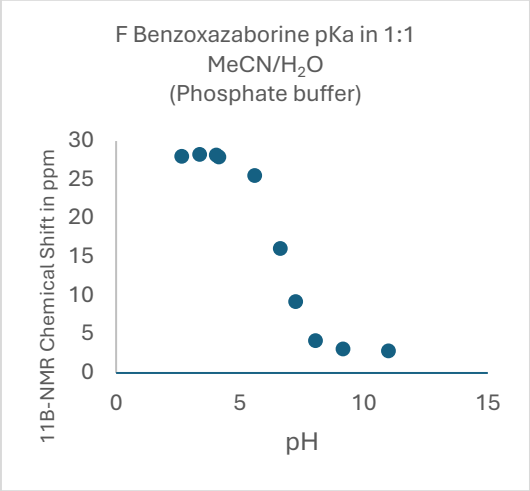


Figure S8: pK_a determination of **BAC 1d** in 1:1 MeCN/H_2O.



1e
pK_a 6.68

Following **GP5**, the pK_a of **BAC 1e** in 1:1 MeCN/H_2O was calculated to be 6.68.



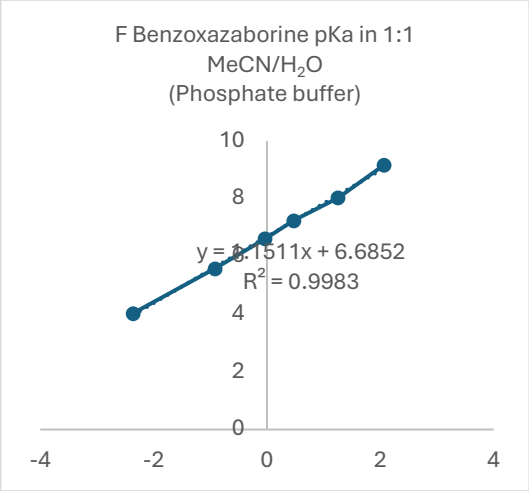


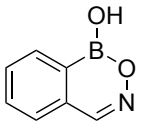
Figure S9: pK_a determination of **BAC 1d** in 1:1 MeCN/H_2O.

6. Kinetic Studies

6.1. Initial Rates Study – NMR Data

General Procedure for Initial Rates Kinetics Study (GP6)

In a small vial, 1*R*,2*R*–1,2-diphenylethanediol (21.4 mg, 0.100 mmol, 1.00 equiv), BAC (0.01 mmol, 10 mol%), 1,3,5–trimethoxybenzene (16.8 mg, 0.100 mmol, 1.00 equiv), and 3 Å powdered molecular sieves were added. 0.7 mL CD_3CN was then added, along with DIPEA (20.0 μL, 0.110 mmol, 1.10 equiv), and $ClP(O)(OEt)_2$ (16 μL, 0.11 mmol, 1.1 equiv). The solution was taken up into an NMR tube and immediately placed in the NMR spectrometer. One ^1H NMR scan was recorded every 2 minutes, for a total duration of 30 minutes. NMR yields were determined using 1,3,5-trimethoxybenzene as the internal standard. For each BAC, this experiment was run in triplicate. A linear regression was then performed, and the determined slope was used in the correlation study of pK_a and initial rates kinetics. Note: time = 0 denotes the time of the initial NMR spectrum being recorded.



1a
pK_a 7.02

Following **GP6**, the initial rates slope for **BAC 1a** was determined to be 1.58.

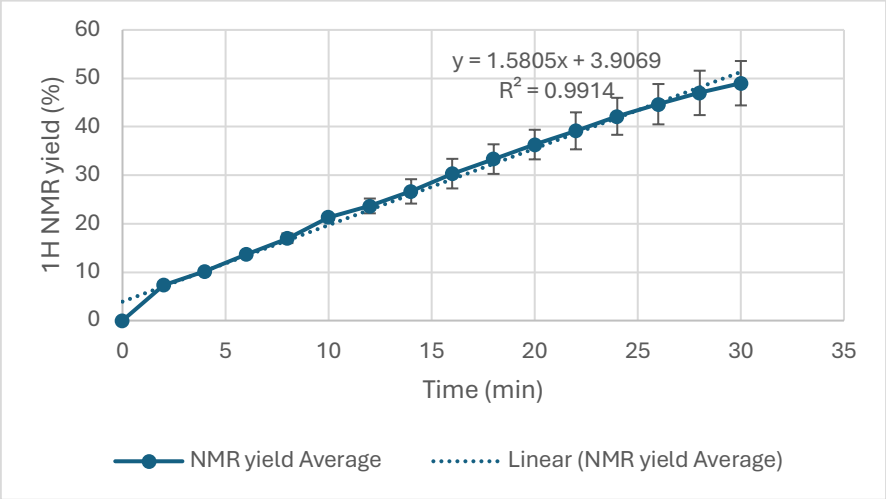
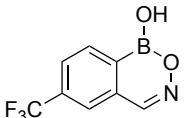


Figure S10: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1a**. Average of triplicate runs shown, with error bars.



1b
pK_a 5.54

Following **GP6**, the initial rates slope for **BAC 1b** was determined to be 0.102.

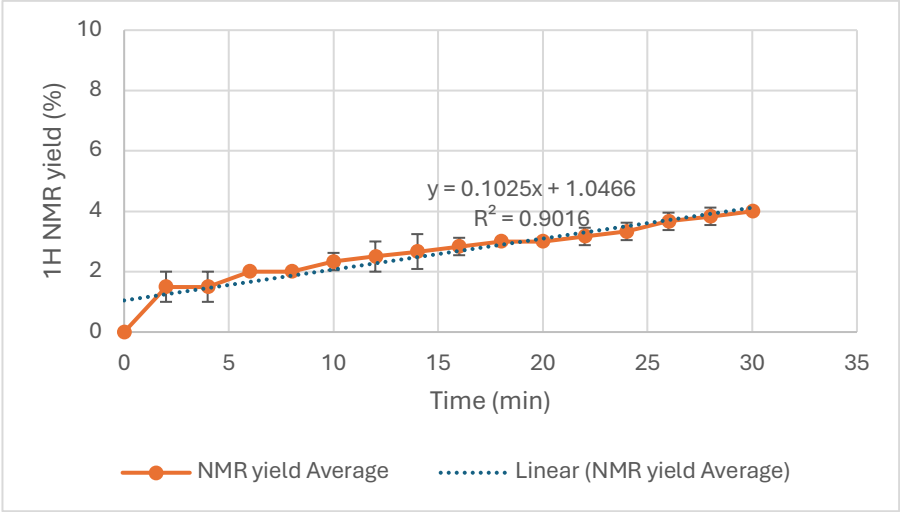
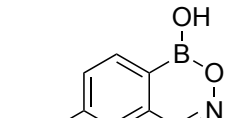


Figure S11: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1b**. Average of triplicate runs shown, with error bars.



1c
pK_a 7.69

Following **GP6**, the initial rates slope for **BAC 1c** was determined to be 1.92.

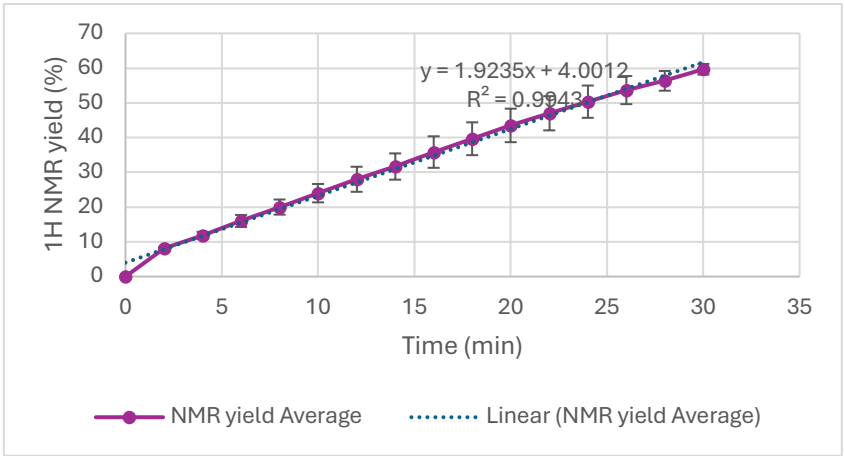
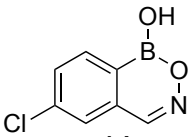


Figure S12: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1c**. Average of triplicate runs shown, with error bars.



1d

pK_a 6.24

Following **GP6**, the initial rates slope for **BAC 1d** was determined to be 1.70.

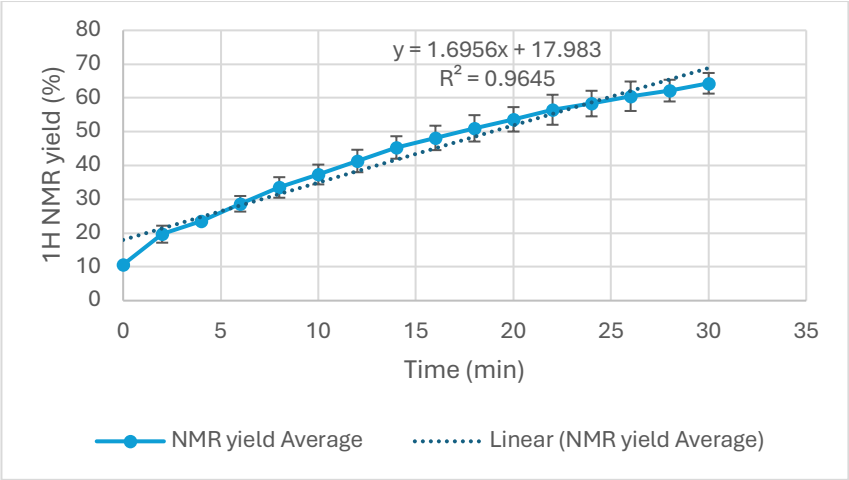
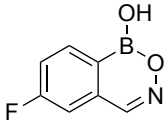


Figure S13: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1d**. Average of triplicate runs shown, with error bars.



1e

pK_a 6.68

Following **GP6**, the initial rates slope for **BAC 1e** was determined to be 1.34.

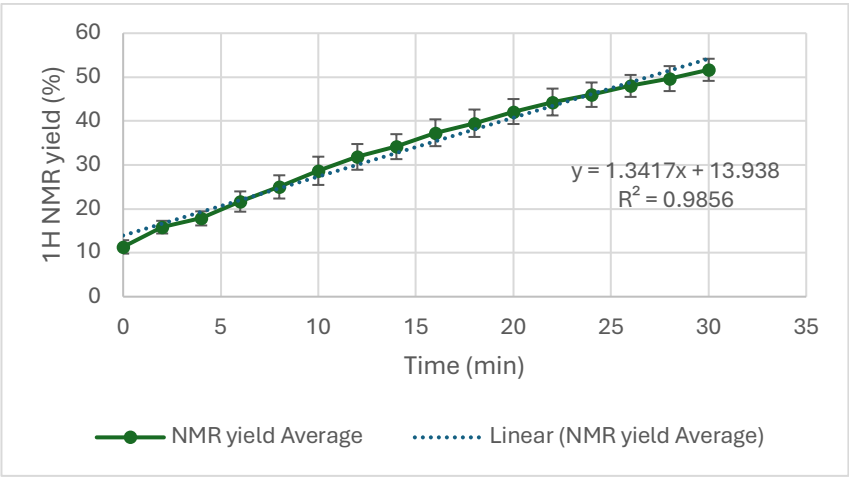


Figure S14: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1e**. Average of triplicate runs shown, with error bars.

No BAC (control experiment)

Following **GP6**, the initial rates slope **without BAC** was determined to be 0.

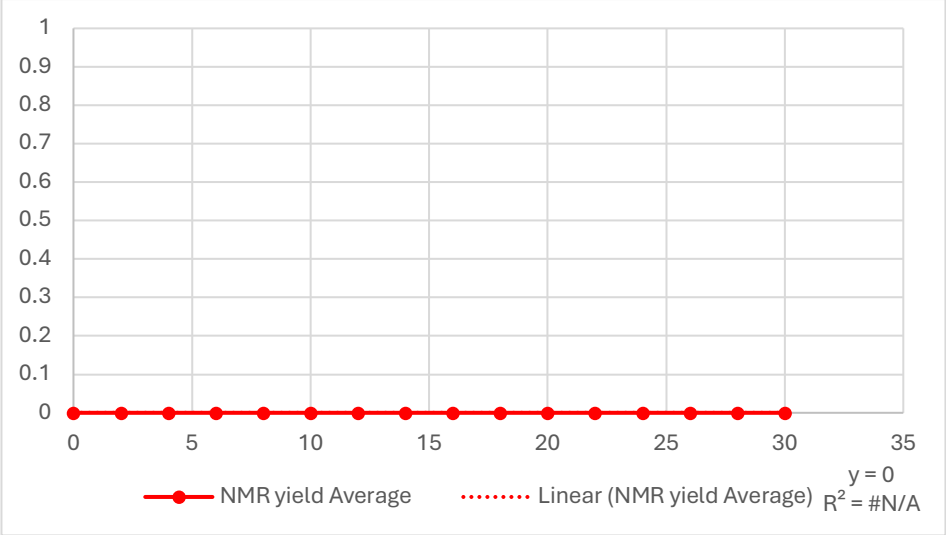


Figure S15: Initial rate study (NMR yield) for the monophosphorylation of 1*R*,2*R*–1,2-diphenylethanediol using **BAC 1e**. Average of triplicate runs shown, with error bars.

6.2. Initial Rates Study – Regression of pK_a vs. Initial Rates

	Catalyst pKa	Initial Rate
BAC 1b (CF_3)	5.54	0.102
BAC 1d (Cl)	6.24	1.70
BAC 1e (F)	6.68	1.34
BAC 1a (H)	7.02	1.58
BAC 1c (OMe)	7.69	1.92

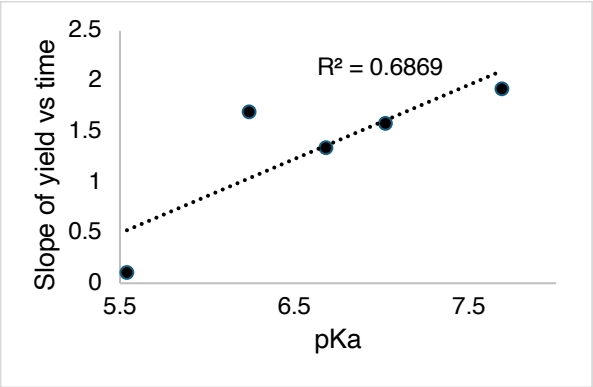
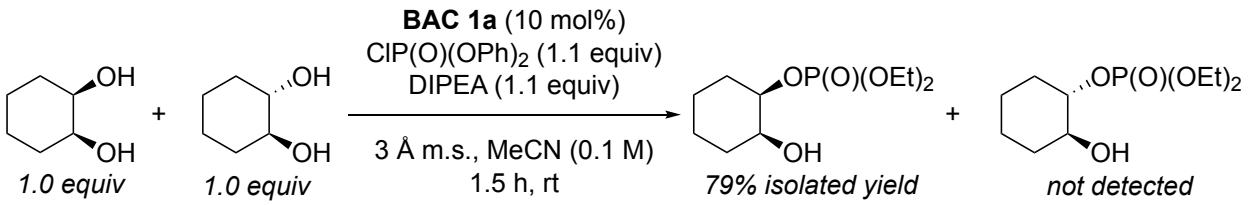


Figure S16: Correlation study between pK_a and Initial rate slope for **BAC 1a**, **BAC 1b**, **BAC 1c**, **BAC 1d**, **BAC 1e**.

7. *cis*– & *trans*–1,2-Cyclohexanediol Competition



In accordance with **GP1**, *cis*–1,2-cyclohexanediol (1.0 equiv) and *trans*–1,2-cyclohexanediol (1.0 equiv) were reacted on a 0.3 mmol scale. Purification was achieved using column chromatography (100% EtOAc). The *cis*–1,2-cyclohexanediol product was the only observed product (60 mg, 79%) as is evident by ^{1}H NMR analysis of the isolated product.

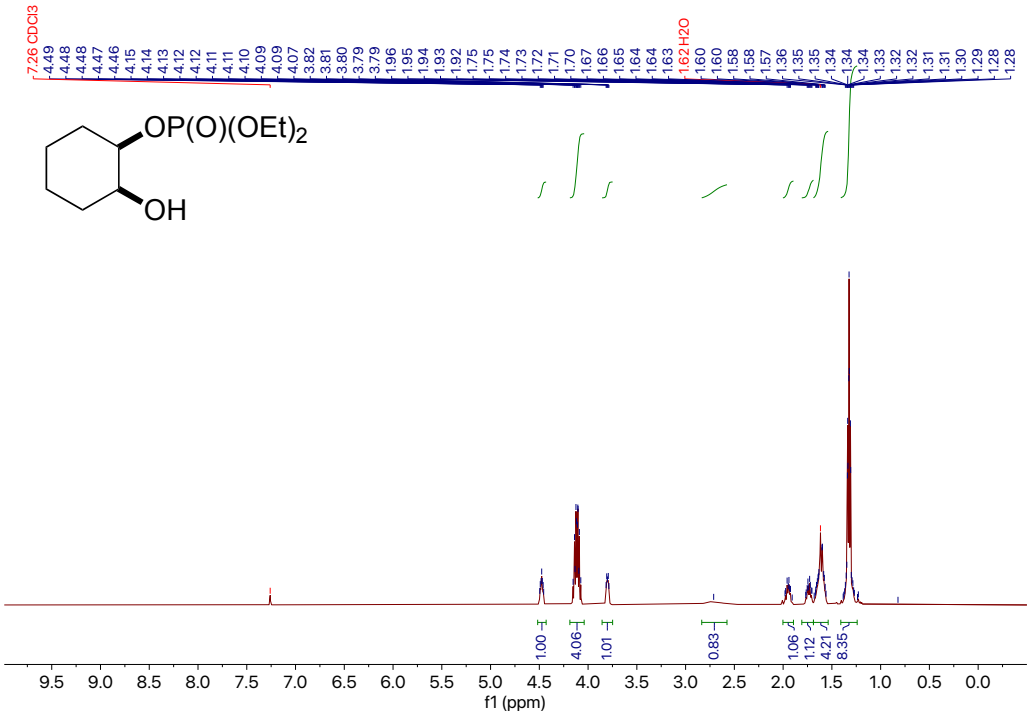


Figure S17: ^{1}H NMR (500 MHz, $CDCl_3$) of isolated monophosphorylated *cis*–1,2-cyclohexanediol product.

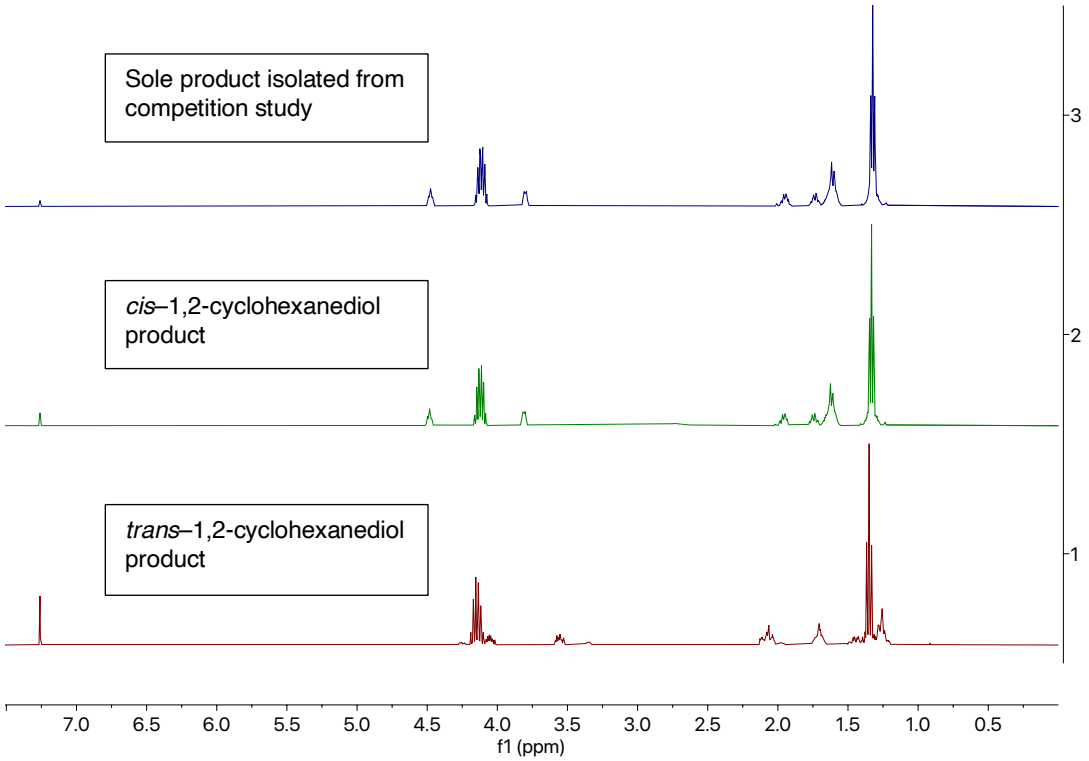
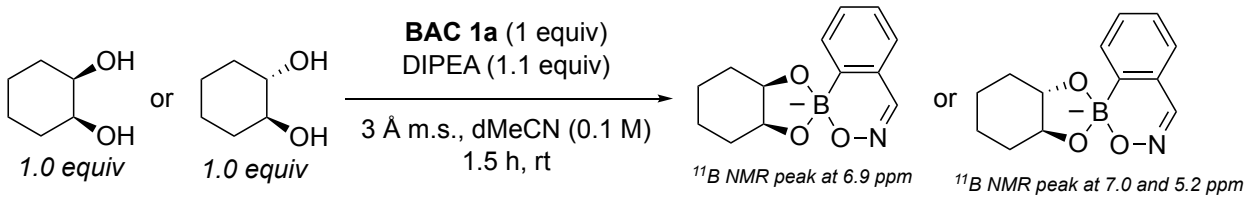


Figure S18: Overlay of ^{1}H (500 MHz, $CDCl_3$) NMR of previously isolated *trans*– and *cis*–1,2-cyclohexanediol product with isolated product from competition study demonstrating that the *cis* product was isolated.

7.1. Complexation Studies with *cis*– *& trans*–1,2-Cyclohexanediol

Stoichiometric complexation experiments were run with either *cis*– *& trans*–1,2-cyclohexanediol, along with 1.0 equiv **BAC 1a**, and 1.1 equiv DIPEA. Contents were stirred in deuterated acetonitrile for 1.5 h and directly transferred into an NMR tube for ^{11}B NMR analysis. Both the *cis*– *& trans*–1,2-cyclohexanediol exhibit ^{11}B NMR peaks with chemical shifts consistent with anionic, tetrahedral boronate complex formation in acetonitrile.



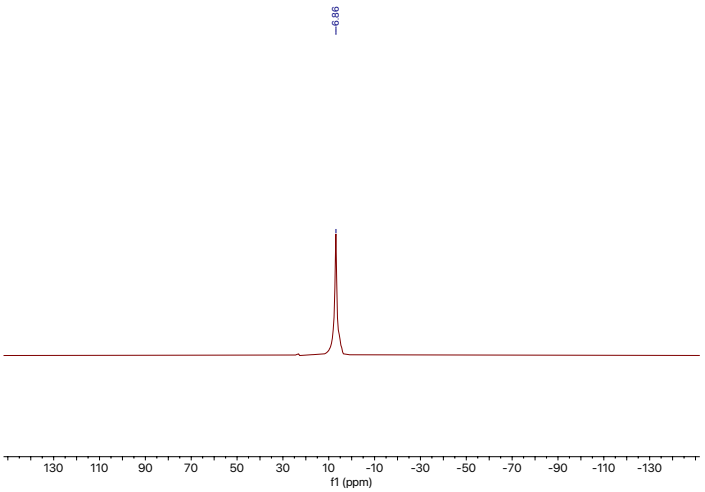


Figure S19: ^{11}B NMR (160 MHz, dMeCN) using *cis*–1,2-cyclohexanediol in the complexation of **BAC 1a**.

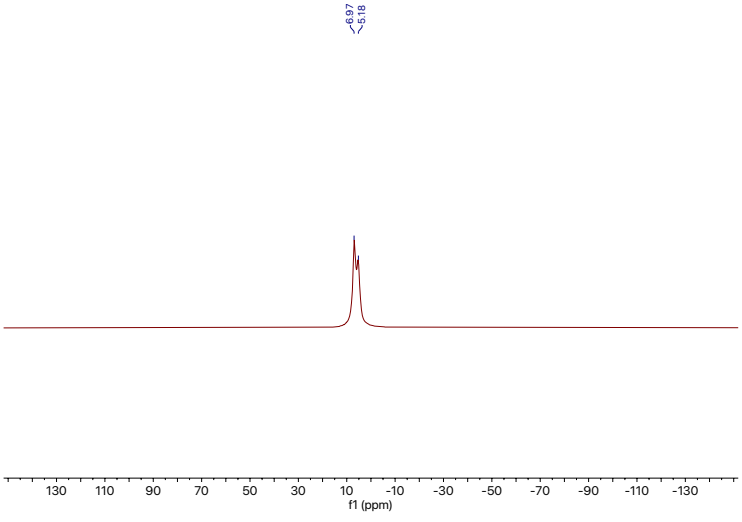


Figure S20: ^{11}B NMR (160 MHz, dMeCN) using *cis*–1,2-cyclohexanediol in the complexation of **BAC 1a**.

8. Computational Methods and Details

The geometry optimizations were performed using the Spartan '24 software package[14] with the ωB97X-D[15] density functional, in combination with the 6-31G(d)[16] basis set for all atoms. The structures were optimized in the gas phase. Harmonic vibrational frequencies were computed for all optimized structures to verify that they were either minima or transition states, possessing zero or one imaginary frequency, respectively. Single points energy calculations were performed using the ωB97X-V[17] density functional, with the 6-311+G(2df,2p) basis set for all atoms. The single points were also performed using a solvation model (SMD) for acetonitrile.[18] All the free energies (SMD(MeCN)/ωB97X-V/6-311+G(2df,2p)//ωB97X-D/6-31G(d)) are reported in kcal mol^{-1}. Condensed Fukui indices[19] of boron-polyol complexes have been previously calculated and employed as a relative measure for the nucleophilic reactivity of atoms. Condensed Fukui functions were calculated according to the method of Yang and Mortier:[20] a single-point energy calculation of the one-electron-oxidized form was carried out, and the difference in Mulliken charges between the adduct and its oxidized form was calculated for each oxygen atom. In obtaining those values, geometry optimizations were performed using the ωB97X-V density functional, in combination with the 6-311+G(2df,2p) basis set for all atoms. Single point energy calculations were additionally performed on the single electron oxidized complex with the same density functional and basis set.

8.1. Data for Reaction Coordinate Diagram

Table S1. Compiled data for Reaction Coordinate Diagram

Computed Species	SCF(M1)	SCF(M2)	ΔG (kcal/mol)
Chloride Anion	-460.235564	-460.315555	
Diethylchlorophosphate	-1185.601072	-1185.724858	
Epimer 1	-1035.128918	-1035.612081	
Epimer 2	-1035.129873	-1035.605719	
Epimer 1-preTS-O4	-2220.777042	-2221.345403	-5.3
Epimer 1-TS-O4	-2220.736473	-2221.340563	3.0
Epimer 1-preTS-O5	-2220.769061	-2221.347934	-6.9
Epimer 1-TS-O5	-2220.738937	-2221.332952	9.4
Epimer 2-preTS-O4	-2220.768452	-2221.344132	-8.5
Epimer 2-TS-O4	-2220.752231	-2221.334001	6.4
Epimer 2-preTS-O5	-2220.768720	-2221.341233	-6.7
Epimer 2-TS-O5	-2220.736473	-2221.330293	6.9
Epimer 1-Product-O4	-1760.514840	-1761.066616	-28.4
Epimer 1-Product-O5	-1760.510797	-1761.069410	-30.1
Epimer 2-Product-O4	-1760.508304	-1761.061278	-29.0
Epimer 2-Product-O5	-1760.502676	-1761.055906	-25.7

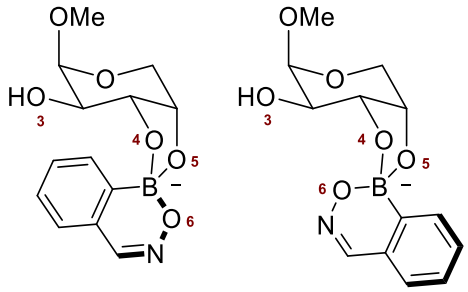
Values are in relation to their respective epimers

SCF(M1): Geometry optimization with ωB97X-D/6-31G(d) theory model in the gas phase (**M1**).

SCF(M2): Single point energy with ωB97X-V/6-311+G(2df,2p) and SMD(MeCN) solvation model (M2).

DG: Relative free energies with respect to the reference molecules.

8.2. Fukui Indices/Mulliken Charge Determination



Epimer 1 Epimer 2

Atom	Mulliken charge	f_k
	Epimer 1	
O-3	-0.348	0.010
O-4	-0.476	0.030
O-5	-0.412	0.041
O-6	-0.206	0.252
	Epimer 2	
O-3	-0.447	0.034
O-4	-0.491	0.044
O-5	-0.412	0.037
O-6	-0.182	0.241

Condensed Fukui indices[19] of boron-polyol complexes have been previously calculated and employed as a relative measure for the nucleophilic reactivity of atoms. Condensed Fukui functions were calculated according to the method of Yang and Mortier:[20] a single-point energy calculation of the one-electron-oxidized form was carried out, and the difference in Mulliken charges between the adduct and its oxidized form was calculated for each oxygen atom. In obtaining those values, geometry optimizations were performed using the ωB97X-V density functional, in combination with the 6-311+G(2df,2p) basis set for all atoms. Single point energy calculations were additionally performed on the single electron oxidized complex with the same density functional and basis set.

In a previous report, condensed Fukui indices were used as a means of explaining the site-selectivity of acylation in a borinic acid-catalyzed system involving carbohydrates.[21] However, in this system, condensed Fukui functions could not properly assess the nucleophilicity of the oxygen atoms as the innate redox potential of this class of boron heterocycles is lower compared to other atoms in the complex. As a result, the largest difference in Mulliken charges upon single electron is on the endocyclic-O6 of the boron heterocycle, not any of the oxygen atoms carbon-bound to the sugar. As was observed experimentally, this oxygen atom is not phosphorylated, and as such, further computational studies are required to elucidate the origin of the observed exquisite selectivity of this methodology.

8.3. Cartesian Coordinates of Optimized Structures for Condensed Fukui Function

Epimer 1-Fukui			
C	-0.998850	-1.605880	-0.202847
H	-1.228099	-0.810488	0.509056
C	1.389337	-0.869142	-0.514383
H	2.171698	-0.821030	-1.292550
C	0.024956	-1.056900	-1.202180
O	1.245952	0.372726	0.114843
O	-0.322961	0.232851	-1.620054
C	-0.436834	-2.775802	0.597711
H	-1.157539	-3.096354	1.363170
C	1.781768	-1.975696	0.445814
O	0.723068	-2.429606	1.294500
B	0.495757	1.203563	-0.866863
O	1.458835	1.813966	-1.856091
C	-0.310170	2.376272	-0.126086
C	-1.473786	4.529354	1.264708
C	-1.586485	2.267976	0.428371
C	0.356662	3.600616	-0.002130
C	-0.216309	4.668827	0.697687
C	-2.166148	3.325917	1.119214
H	-2.136141	1.337563	0.306459
H	0.323029	5.610208	0.784331
H	-3.158506	3.218804	1.549384
H	-1.922235	5.355596	1.809698
N	2.136688	2.952232	-1.562715
C	1.641340	3.750683	-0.687244
H	2.227571	4.656200	-0.527227
H	2.172703	-2.828308	-0.126875
O	-0.222132	-3.844240	-0.308223
C	0.129830	-5.048821	0.334061
H	1.077682	-4.953368	0.872684
H	0.227270	-5.813003	-0.437564
H	-0.647501	-5.353911	1.047624
H	0.088151	-1.739183	-2.063145
H	2.560553	-1.611817	1.118646
O	-2.228756	-1.981153	-0.805953
H	-2.020398	-2.658654	-1.455828

SCF energy: -1035.525774
ωB97X-V (Gas Phase) / 6-311+G (2df,2p) opt.
No imaginary frequency

Epimer 2-Fukui			
C	1.072257	-1.897621	0.537049
C	1.332110	0.548946	0.135231
C	0.945269	-0.787282	-0.498888
O	0.173289	0.924354	0.822237
O	-0.405496	-0.622612	-0.853833
C	2.460192	-1.906164	1.160505
H	2.540735	-2.703814	1.912502
C	2.572194	0.460587	1.015910
O	2.651126	-0.704830	1.842045
B	-1.001756	0.308426	0.135268
C	-1.964975	1.408700	-0.531858
C	-3.685570	3.425309	-1.483736
C	-3.113870	1.771577	0.177616
C	-1.710168	2.064101	-1.739057
C	-2.552713	3.061543	-2.214130
C	-3.967298	2.777719	-0.291562
H	-0.833203	1.777346	-2.314374
H	-2.333217	3.562079	-3.153726
H	-4.854728	3.042186	0.279125
H	-4.345144	4.206485	-1.851375
O	-1.777367	-0.503403	1.134077
N	-2.830249	-0.017926	1.834709
C	-3.422243	1.035130	1.402828
H	-4.269885	1.347195	2.010218
H	2.587906	1.306217	1.705874
H	1.544149	-1.039831	-1.381688
O	3.500830	-2.063831	0.207951
C	3.824548	-3.406247	-0.082380
H	4.704331	-3.387814	-0.728238
H	3.004197	-3.922355	-0.589121
H	4.073959	-3.955851	0.837739
O	0.772176	-3.164349	-0.042809
H	-0.089454	-3.040588	-0.457784
H	3.464536	0.500812	0.378081
H	1.565452	1.279397	-0.663085
H	0.368080	-1.683591	1.348680

SCF energy: -1035.525875
ωB97X-V (Gas Phase) / 6-311+G (2df,2p) opt.
No imaginary frequency

8.4 Cartesian Coordinates of Optimized Structures for Reaction Coordinate Diagram

Diethylchlorophosphate

P	0.839927	-0.534009	-0.901044
O	2.254469	-0.282418	-0.585425
O	0.061763	-1.647029	-0.078658
O	-0.135499	0.722257	-0.767480
C	0.163975	-1.620324	1.365891
H	1.221988	-1.649884	1.641569
H	-0.272524	-0.683076	1.726108
C	-0.588516	-2.820323	1.894800
H	-0.153146	-3.746047	1.509282
H	-1.639961	-2.777186	1.598592
H	-0.533028	-2.836640	2.987708
C	0.323568	2.015249	-1.219340
H	1.263390	2.250700	-0.712633
H	0.509899	1.962932	-2.297847
C	-0.759956	3.021896	-0.902312
H	-0.951393	3.055635	0.173861
H	-1.689808	2.762825	-1.415693
H	-0.444986	4.017165	-1.230658
Cl	0.529838	-1.211722	-2.786720

SCF energy: -1185.601072
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 1

C	-0.998706	-1.602342	-0.209751
H	-1.234550	-0.808556	0.500483
C	1.399654	-0.868508	-0.509839
H	2.182563	-0.836927	-1.287507
C	0.033246	-1.048260	-1.201572
O	1.270941	0.376946	0.106405
O	-0.304123	0.239547	-1.618790
C	-0.439620	-2.770109	0.598964
H	-1.161280	-3.079653	1.366696
C	1.780870	-1.975484	0.454595
O	0.719191	-2.430843	1.293777
B	0.513461	1.208131	-0.865369
O	1.476154	1.826262	-1.856693
C	-0.293574	2.374468	-0.123062
C	-1.478544	4.515119	1.268882
C	-1.563318	2.250407	0.441311
C	0.357652	3.609692	-0.009580
C	-0.228005	4.671744	0.690733
C	-2.153826	3.301319	1.133836
H	-2.099207	1.312557	0.325097
H	0.295735	5.621710	0.768903
H	-3.140448	3.180762	1.572356
H	-1.934819	5.336448	1.813596
N	2.131381	2.975589	-1.581250
C	1.629322	3.774123	-0.706091
H	2.202474	4.688001	-0.560722
H	2.175319	-2.827433	-0.116230
O	-0.235431	-3.844464	-0.300371
C	0.103692	-5.051280	0.334318
H	1.047894	-4.964833	0.883978
H	0.206078	-5.809254	-0.444018
H	-0.682274	-5.362144	1.037870
H	0.101287	-1.728464	-2.062600
H	2.554770	-1.614652	1.132892
O	-2.222134	-1.977516	-0.816166
H	-2.011823	-2.662103	-1.455080

SCF energy: -1035.128918
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 2

C	1.075922	-1.905163	0.542217
C	1.330435	0.547881	0.133440
C	0.938857	-0.792830	-0.493816
O	0.173404	0.937559	0.807920
O	-0.407941	-0.626315	-0.846552
C	2.465048	-1.902928	1.167253
H	2.544121	-2.693841	1.925535
C	2.570449	0.461394	1.015158
O	2.655457	-0.700981	1.839770
B	-1.000934	0.314450	0.131007
C	-1.967371	1.407692	-0.534687
C	-3.683788	3.430280	-1.482294
C	-3.117659	1.770748	0.177132
C	-1.710785	2.065695	-1.739365
C	-2.550728	3.066616	-2.212764
C	-3.968672	2.779938	-0.292344
H	-0.833318	1.779538	-2.312772
H	-2.328783	3.569830	-3.149799
H	-4.856616	3.045382	0.276698
H	-4.341189	4.213555	-1.847803
O	-1.771399	-0.494847	1.143386
N	-2.831416	-0.019229	1.831654
C	-3.428158	1.032790	1.395502
H	-4.281353	1.336580	1.999111
H	2.585825	1.307070	1.703795
H	1.535173	-1.046052	-1.377383
O	3.507597	-2.066545	0.220055
C	3.820768	-3.402709	-0.087916
H	4.700518	-3.380176	-0.734632
H	2.996541	-3.905426	-0.602061
H	4.068089	-3.970180	0.822517
O	0.784649	-3.172714	-0.032244
H	-0.076800	-3.058956	-0.444761
H	3.461344	0.502684	0.375492
H	1.571083	1.267875	-0.671619
H	0.371628	-1.698663	1.355169

SCF energy: -1035.129873
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 1-preTS-O4

C	2.060697	-0.841471	0.398426
H	1.414995	-1.267815	1.179307
C	1.612119	1.523435	1.207426
H	1.593206	2.551595	0.801856
C	1.481506	0.528605	0.037655
O	0.465502	1.284418	1.973460
O	0.098771	0.437341	-0.174300
C	3.435218	-0.689200	1.043406
H	3.825767	-1.670732	1.350789
C	2.896353	1.389975	2.016449
O	3.338094	0.054263	2.232570
B	-0.607537	0.987804	1.030962
O	-1.263144	2.282181	0.616969
C	-1.716466	-0.022465	1.594015
C	-3.780361	-1.763897	2.401703
C	-1.456175	-1.107817	2.435269
C	-3.039080	0.179128	1.172691
C	-4.066285	-0.686722	1.573920
C	-2.468682	-1.974700	2.835425
H	-0.437884	-1.262751	2.786307
H	-5.086416	-0.508548	1.237351
H	-2.242920	-2.816920	3.485968
H	-4.574070	-2.440019	2.711016
N	-2.522767	2.334499	0.115116
C	-3.320652	1.351453	0.352629
H	-4.315737	1.477172	-0.072654
H	3.692045	1.958212	1.513060
O	4.309613	-0.100481	0.116899
C	5.639830	-0.059099	0.561573
H	5.750988	0.552873	1.466742
H	6.234582	0.376263	-0.245561
H	6.019343	-1.070078	0.779926
H	1.984154	0.894564	-0.868214
H	2.737655	1.814181	3.010765
O	2.127561	-1.734732	-0.686943
H	1.779128	-1.288815	-1.479116
P	-0.649667	-0.389852	-3.026025
Cl	-1.316106	-1.086403	-4.853218
O	-1.232010	1.072923	-3.080607
O	-1.586215	-1.190016	-2.042879
C	-1.051124	-2.238609	-1.191223
H	-0.539124	-1.742886	-0.368465
H	-0.326624	-2.829966	-1.758507
C	-2.220028	-3.070357	-0.720701
H	-1.859951	-3.835058	-0.024742
H	-2.720787	-3.561763	-1.561601
H	-2.938645	-2.441647	-0.189643
C	-0.440086	2.212967	-2.633705
H	-0.183653	2.051564	-1.587068
H	0.465487	2.250261	-3.247538
C	-1.301146	3.442362	-2.802496
H	-2.166928	3.373894	-2.138737
H	-1.627186	3.561667	-3.841324
H	-0.719265	4.323688	-2.511413
O	0.814104	-0.574468	-2.932968

SCF energy: -2220.777042
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 1-TS-O4

C	2.334465	-0.223308	0.388964
H	1.781942	-1.010807	0.916967
C	1.234374	1.556183	1.807472
H	0.890938	2.602231	1.749478
C	1.458252	1.030483	0.383814
O	0.222623	0.738160	2.327777
O	0.119783	0.740798	-0.022186
C	3.590186	0.045675	1.220766
H	4.206605	-0.862986	1.272788
C	2.484841	1.528932	2.672542
O	3.255782	0.342432	2.553414
B	-0.833202	0.612028	1.364563
O	-1.691123	1.783193	1.342404
C	-1.618704	-0.758006	1.357105
C	-3.155628	-3.102112	1.179349
C	-1.045607	-2.007882	1.604226
C	-2.982079	-0.700561	1.048905
C	-3.748941	-1.869811	0.954284
C	-1.799091	-3.170956	1.516260
H	0.008723	-2.063000	1.864626
H	-4.805724	-1.805594	0.701988
H	-1.336276	-4.137900	1.699745
H	-3.744191	-4.012703	1.099498
N	-3.020539	1.757872	1.016473
C	-3.585361	0.613102	0.869585
H	-4.641131	0.679510	0.610125
H	3.105386	2.401790	2.424969
O	4.310076	1.081103	0.610436
C	5.573029	1.296136	1.187448
H	5.494890	1.612089	2.236354
H	6.059991	2.083110	0.606568
H	6.189517	0.384869	1.144807
H	1.880950	1.786335	-0.280027
H	2.189031	1.591413	3.722036
O	2.698667	-0.692659	-0.884069
H	2.344602	-0.075471	-1.552800
P	-0.263145	0.368161	-1.777400
Cl	-1.085551	-0.096453	-4.170013
O	-1.657418	1.103578	-1.620809
O	-0.522430	-1.151217	-1.440397
C	0.111271	-2.245834	-2.124330
H	0.923657	-2.584387	-1.475227
H	0.524770	-1.891606	-3.071033
C	-0.940722	-3.308988	-2.354211
H	-0.476173	-4.205940	-2.781311
H	-1.691810	-2.926605	-3.050691
H	-1.426711	-3.574543	-1.409580
C	-1.728289	2.503321	-1.935568
H	-1.381327	3.059474	-1.057594
H	-1.076298	2.708322	-2.790295
C	-3.170277	2.823693	-2.267380
H	-3.806792	2.614383	-1.404131
H	-3.492085	2.218989	-3.120408
H	-3.262924	3.885963	-2.523338
O	0.995198	0.926002	-2.342937

SCF energy: -2220.736473
ωB97X-D (Gas Phase) / 6-31G (d) opt.
1 imaginary frequency: 120i cm^{-1}

Epimer 1-preTS-O5

C	-2.434669	-1.402730	-0.708681
H	-2.344295	-0.485640	-0.122803
C	0.023227	-1.524606	-1.223446
H	0.721969	-1.829476	-2.024645
C	-1.380667	-1.352597	-1.827428
O	0.311970	-0.235290	-0.772637
O	-1.335341	-0.097560	-2.437513
C	-2.189966	-2.563922	0.252087
H	-2.897088	-2.516680	1.093135
C	0.141823	-2.556687	-0.115012
O	-0.922471	-2.520408	0.834545
B	-0.312151	0.704733	-1.758779
O	0.733434	1.102068	-2.757040
C	-0.826391	2.017343	-0.991788
C	-1.394203	4.332923	0.507710
C	-2.115121	2.263557	-0.512020
C	0.159268	2.987995	-0.756543
C	-0.115962	4.132177	0.002738
C	-2.401847	3.405013	0.233168
H	-2.906323	1.551169	-0.737651
H	0.670434	4.861255	0.188363
H	-3.409316	3.574300	0.607800
H	-1.612590	5.216574	1.102873
N	1.704718	1.982838	-2.381625
C	1.445207	2.807740	-1.423407
H	2.266795	3.480828	-1.181754
H	0.200197	-3.561861	-0.557170
O	-2.412917	-3.754608	-0.476398
C	-2.383276	-4.909019	0.325479
H	-1.399196	-5.054089	0.787928
H	-2.609703	-5.758843	-0.323359
H	-3.138090	-4.855841	1.125556
H	-1.610284	-2.131677	-2.569861
H	1.053037	-2.366543	0.457354
O	-3.765410	-1.444197	-1.185279
H	-3.839083	-2.275625	-1.672204
P	2.925365	0.840032	2.116301
Cl	4.457069	0.319385	3.387371
O	1.723829	0.202561	2.915387
O	3.117955	-0.143384	0.885651
C	3.883046	0.285521	-0.266443
H	4.944832	0.228140	0.003696
H	3.620204	1.318393	-0.500233
C	0.386180	0.222054	2.308834
H	-0.095365	-0.671579	2.709275
H	0.468876	0.107667	1.223711
C	-0.348874	1.489384	2.681695
H	0.162181	2.364763	2.272771
H	-0.434626	1.596311	3.768452
H	-1.350770	1.461866	2.242162
C	3.540876	-0.622012	-1.424081
H	3.725376	-1.670596	-1.165917
H	4.161654	-0.353381	-2.284820
H	2.494575	-0.480287	-1.698995
O	2.941899	2.282548	1.823492

SCF energy: -2220.769061
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 1-TS-O5

C	-2.365522	-1.242594	-0.532316
H	-2.361708	-0.330240	0.069049
C	0.139835	-1.276224	-0.751107
H	0.959449	-1.477903	-1.451021
C	-1.182094	-1.166493	-1.511375
O	0.283425	0.069452	-0.275576
O	-1.146438	0.061558	-2.163834
C	-2.218260	-2.419026	0.430994
H	-3.002729	-2.384765	1.200323
C	0.135682	-2.382227	0.290204
O	-1.012259	-2.387828	1.130375
B	-0.174099	0.973226	-1.602982
O	1.001346	1.045050	-2.455266
C	-0.737601	2.391839	-1.178788
C	-1.585111	4.994341	-0.533035
C	-1.993960	2.616192	-0.612476
C	0.073305	3.501517	-1.447603
C	-0.344780	4.796445	-1.124165
C	-2.415064	3.900261	-0.281038
H	-2.659888	1.773263	-0.445496
H	0.305647	5.643387	-1.334336
H	-3.393046	4.054879	0.169771
H	-1.911084	5.998534	-0.272332
N	1.799044	2.158366	-2.569425
C	1.357803	3.265908	-2.093260
H	2.044477	4.100472	-2.226377
H	0.185790	-3.329302	-0.267026
O	-2.368628	-3.592325	-0.341470
C	-2.409648	-4.768143	0.432238
H	-1.480533	-4.909083	0.996978
H	-2.546387	-5.602378	-0.259770
H	-3.250544	-4.745663	1.142257
H	-1.273079	-1.984864	-2.240732
H	0.994191	-2.321281	0.954222
O	-3.618615	-1.299467	-1.177309
H	-3.643309	-2.158597	-1.619838
P	1.704542	0.556809	0.858002
Cl	3.614877	0.879558	2.546156
O	1.028054	-0.292002	2.025262
O	2.675387	-0.446546	0.096403
C	3.789356	0.090344	-0.650256
H	4.470402	0.557534	0.066127
H	3.417814	0.838179	-1.356548
C	0.268778	0.426794	3.005964
H	-0.558666	0.944315	2.505380
H	0.926271	1.164773	3.475688
C	-0.238767	-0.593774	4.003112
H	0.605371	-1.077754	4.504168
H	-0.829150	-1.356705	3.487519
H	-0.862306	-0.101503	4.757879
C	4.431361	-1.075319	-1.370773

H	4.779718	-1.826367	-0.654498
H	5.289560	-0.719787	-1.951188
H	3.719913	-1.542142	-2.060303
O	1.581875	2.007308	0.663446

SCF energy: -2220.738937
ωB97X-D (Gas Phase) / 6-31G (d) opt.
1 imaginary frequency: 145i cm^{-1}

Epimer 2-preTS-O4

C	-1.099025	-1.014570	1.765089
C	1.211682	-1.666644	0.934615
C	-0.094622	-0.926786	0.613592
O	1.973551	-0.731762	1.633316
O	0.312222	0.398938	0.423627
C	-1.228348	-2.442182	2.279762
H	-1.883299	-2.467645	3.161115
C	0.997288	-2.971676	1.694119
O	0.005963	-2.917152	2.713224
B	1.499749	0.623500	1.309050
C	2.547300	1.569060	0.540415
C	4.204183	3.383235	-0.846039
C	2.711551	2.886882	0.989563
C	3.242936	1.182052	-0.609267
C	4.056989	2.070586	-1.304689
C	3.538866	3.787865	0.302473
H	3.127205	0.162104	-0.972339
H	4.578810	1.749622	-2.203846
H	3.648471	4.807486	0.669168
H	4.837823	4.083221	-1.385914
O	1.076563	1.250196	2.606103
N	1.242035	2.550009	2.932517
C	1.985437	3.292031	2.185960
H	2.071178	4.321182	2.534395
H	1.923136	-3.252651	2.201645
H	-0.562324	-1.308913	-0.300345
O	-1.756629	-3.304145	1.281972
C	-3.120009	-3.595349	1.443557
H	-3.394386	-4.299020	0.651746
H	-3.739356	-2.694038	1.361132
H	-3.316589	-4.073638	2.416851
O	-2.387147	-0.564593	1.382913
H	-2.276492	0.270074	0.893916
H	0.731222	-3.762681	0.978243
H	1.709240	-1.937905	-0.018698
H	-0.709724	-0.408022	2.592070
P	-2.265113	0.932641	-2.128946
O	-2.638003	1.366635	-0.771424
O	-1.087059	1.630465	-2.899703
O	-1.971606	-0.618484	-2.329504
C	-2.840698	-1.597744	-1.707591
H	-3.843292	-1.481222	-2.137098
H	-2.872488	-1.407546	-0.630642
C	0.205574	1.887677	-2.245614
H	0.421869	1.091387	-1.529211
H	0.917177	1.857846	-3.072441
C	0.188874	3.230465	-1.555019
H	-0.157454	4.015959	-2.235302
H	1.203470	3.467531	-1.221875
H	-0.458477	3.193591	-0.675082
C	-2.271266	-2.965466	-2.011385
H	-2.138496	-3.101207	-3.089139
H	-2.959685	-3.732466	-1.642977
H	-1.313440	-3.105557	-1.504412
Cl	-3.785336	1.286825	-3.463647

SCF energy: -2220.768452
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 2-TS-O4

C	2.525486	-0.061876	0.263917
C	1.671261	2.246393	0.763387
C	1.701463	1.113384	-0.268294
O	0.698765	1.828449	1.686834
O	0.310422	0.781225	-0.369115
C	3.895063	0.453917	0.720392
H	4.492921	-0.390889	1.094838
C	3.011753	2.507194	1.434308
O	3.730090	1.331964	1.788224
B	-0.446494	1.338924	0.968089
C	-1.248467	0.173080	1.690463
C	-2.813800	-1.889793	2.792818
C	-2.647859	0.223514	1.637822
C	-0.654831	-0.905793	2.351134
C	-1.421051	-1.930396	2.895330
C	-3.427391	-0.808318	2.177253
H	0.428009	-0.940520	2.436381
H	-0.938248	-2.768178	3.392739
H	-4.512700	-0.755550	2.112700
H	-3.416147	-2.695563	3.205179
O	-1.306151	2.441614	0.527051
N	-2.665612	2.429338	0.553941
C	-3.263761	1.400902	1.042957
H	-4.350316	1.478152	1.024683
H	2.837429	3.040957	2.371189
H	2.059860	1.421935	-1.250356
O	4.607186	1.130295	-0.289432
C	5.175369	0.319188	-1.293924
H	4.421203	-0.073214	-1.980013
H	5.719453	-0.530742	-0.854105
H	5.884139	0.952179	-1.835812
O	2.732567	-1.106684	-0.656347
H	1.858441	-1.429297	-0.930349
H	3.630141	3.129992	0.776664
H	1.355413	3.178232	0.267218
H	2.029954	-0.436504	1.170258
P	-0.325370	-0.043116	-1.960332
O	0.605700	0.655624	-2.862851
O	0.022722	-1.466712	-1.299430
O	-1.791847	0.383464	-1.526845
C	-2.569039	1.269459	-2.359567
H	-2.117813	1.322074	-3.352881
H	-2.531393	2.249035	-1.878923
C	-0.981230	-2.373535	-0.807947
H	-1.628933	-1.841488	-0.106945
H	-1.568505	-2.713133	-1.664039
C	-0.248730	-3.507027	-0.123867
H	0.396441	-4.033965	-0.833605
H	-0.973285	-4.216441	0.289329
H	0.364357	-3.125299	0.697925
C	-3.980282	0.730247	-2.435958
H	-3.979115	-0.238599	-2.942745
H	-4.610471	1.431258	-2.996534
H	-4.397142	0.615871	-1.430467
Cl	-1.349627	-1.295229	-3.822338

SCF energy: -2220.752231
ωB97X-D (Gas Phase) / 6-31G (d) opt.
1 imaginary frequency: 95i cm^{-1}

Epimer 2-preTS-O5

C	-1.396233	0.223889	2.727128
C	-1.135863	0.955147	0.348366
C	-0.917069	1.349322	1.812521
O	-0.025129	0.154206	0.074929
O	0.473676	1.503763	1.936619
C	-2.837998	-0.150223	2.400409
H	-3.187183	-0.958040	3.062198
C	-2.468279	0.256090	0.090498
O	-2.874161	-0.663827	1.105454
B	1.091992	0.561624	0.992394
C	2.292682	1.147536	0.111369
C	4.225144	1.839910	-1.814128
C	3.206159	0.195973	-0.368855
C	2.389397	2.455300	-0.369164
C	3.340574	2.805111	-1.323545
C	4.164850	0.539295	-1.330920
H	1.689767	3.200716	0.003964
H	3.393011	3.825584	-1.697953
H	4.852094	-0.217529	-1.704354
H	4.961190	2.107036	-2.568819
O	1.548669	-0.650932	1.738080
N	2.402881	-1.549128	1.168457
C	3.129706	-1.154592	0.180887
H	3.776474	-1.928497	-0.228329
H	-2.393271	-0.335949	-0.823744
H	-1.427666	2.280027	2.089954
O	-3.740449	0.934977	2.470605
C	-4.131163	1.290950	3.774018
H	-4.927529	2.033824	3.670245
H	-3.301040	1.709584	4.350988
H	-4.529391	0.420804	4.321449
O	-1.238907	0.585574	4.089510
H	-0.318366	0.885421	4.132436
H	-3.252046	1.014897	-0.032239
H	-1.122236	1.863395	-0.285491
H	-0.794998	-0.668463	2.511421
P	-0.033187	-1.965041	-2.640007
O	-0.487543	-0.464593	-2.897940
O	-0.974900	-2.557282	-1.516981
Cl	-0.886292	-2.873460	-4.279121
O	1.413592	-2.217480	-2.538633
C	0.506012	0.593824	-2.850953
H	1.233821	0.373787	-2.074787

H	-0.057322	1.477361	-2.545716
C	-0.428389	-2.872989	-0.194127
H	-0.215801	-1.927884	0.303853
H	0.501489	-3.429162	-0.330896
C	1.169011	0.776566	-4.199631
H	0.432679	0.975137	-4.985493
H	1.740367	-0.118642	-4.462646
H	1.866475	1.618940	-4.136780
C	-1.483291	-3.668900	0.536876
H	-2.386445	-3.065448	0.658301
H	-1.102313	-3.922126	1.532148
H	-1.727250	-4.595389	0.006170

SCF energy: -2220.768720
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 2-TS-O5

C	-1.419584	-0.056626	2.495766
C	-1.162272	0.917802	0.202849
C	-0.906250	1.137673	1.690905
O	-0.042270	0.091224	-0.146489
O	0.480015	1.271809	1.838010
C	-2.893841	-0.298707	2.189172
H	-3.265751	-1.165145	2.755253
C	-2.570318	0.379552	-0.054049
O	-3.005080	-0.633594	0.841004
B	1.199073	0.355352	0.983508
C	2.479680	0.963953	0.289927
C	4.835975	1.864396	-0.941441
C	3.584348	0.115952	0.149889
C	2.584509	2.276323	-0.175432
C	3.746544	2.726464	-0.794288
C	4.759176	0.563620	-0.463567
H	1.740697	2.951255	-0.045332
H	3.811414	3.747555	-1.162389
H	5.605117	-0.112146	-0.570943
H	5.744231	2.212681	-1.427089
O	1.420904	-0.924138	1.613165
N	2.507837	-1.730802	1.365794
C	3.476344	-1.234717	0.686076
H	4.299272	-1.931207	0.535080
H	-2.666395	-0.041965	-1.051910
H	-1.401110	2.046732	2.050499
O	-3.716613	0.819490	2.442317
C	-4.070232	1.004331	3.793051
H	-4.853229	1.768255	3.808438
H	-3.217952	1.328867	4.398074
H	-4.472741	0.075585	4.228764
O	-1.203910	0.151743	3.877492
H	-0.256021	0.339786	3.941506
H	-3.240473	1.245928	0.028801
H	-1.064230	1.860982	-0.350904
H	-0.887131	-0.956455	2.164459
P	0.061515	-0.895769	-1.669267
O	-0.614084	0.251703	-2.546078
O	-1.131289	-1.834091	-1.233143
Cl	-0.121815	-2.379759	-3.966337
O	1.494647	-1.205640	-1.622352
C	0.246359	1.318480	-2.991174
H	0.963543	1.565193	-2.198546
H	-0.426841	2.172111	-3.124352
C	-0.817627	-3.162596	-0.767170
H	-0.175984	-3.077915	0.117486
H	-0.282988	-3.677625	-1.570396
C	0.962937	0.963178	-4.280079
H	0.242698	0.709925	-5.061942
H	1.606592	0.093021	-4.128364
H	1.569984	1.819485	-4.600394
C	-2.139568	-3.824580	-0.443914
H	-2.694843	-3.223114	0.282300
H	-1.963684	-4.822846	-0.027924
H	-2.739287	-3.920970	-1.354321

SCF energy: -2220.736473
ωB97X-D (Gas Phase) / 6-31G (d) opt.
1 imaginary frequency: 115i cm^{-1}

Epimer 1-Product-O4

C	2.355295	-0.361024	0.078239
H	1.882877	-1.204629	0.589781
C	0.968901	1.249600	1.421217
H	0.385645	2.175338	1.357598
C	1.355590	0.789546	0.015128
O	0.198383	0.232238	2.037607
O	0.169198	0.366817	-0.655993
C	3.555151	0.079252	0.923300
H	4.253687	-0.755669	1.062595
C	2.225115	1.514735	2.242806
O	3.143232	0.436142	2.220819
B	-1.145052	0.167532	1.825282
O	-1.808249	1.294367	1.378498
C	-1.961680	-1.106090	2.117198
C	-3.657205	-3.293478	2.509289
C	-1.450354	-2.314384	2.603229
C	-3.330852	-1.010533	1.828296
C	-4.181029	-2.105987	2.024164
C	-2.291512	-3.399288	2.799427
H	-0.389632	-2.393456	2.822549
H	-5.240261	-2.023071	1.795373
H	-1.893432	-4.336588	3.176430
H	-4.309046	-4.148139	2.663656
N	-3.167834	1.333051	1.098977
C	-3.832228	0.254851	1.315375
H	-4.888376	0.351581	1.073258
H	2.700506	2.432136	1.870708
O	4.173823	1.131399	0.244781
C	5.421365	1.506026	0.790500
H	5.315738	1.871691	1.818753
H	5.816652	2.301927	0.157293
H	6.120754	0.658361	0.785834
H	1.807517	1.629207	-0.523162
H	1.952068	1.657783	3.289712
O	2.741746	-0.818618	-1.191982
H	2.814448	-0.054041	-1.785830
P	0.017915	0.569962	-2.251316
O	-1.324595	1.403920	-2.391649
O	-0.519907	-0.814143	-2.801823
C	0.414758	-1.850553	-3.172089
H	0.956325	-2.171249	-2.279289
H	1.138612	-1.432724	-3.878215
C	-0.382650	-2.977115	-3.790773
H	0.291828	-3.786734	-4.086780
H	-0.920525	-2.628246	-4.676671
H	-1.108999	-3.373359	-3.075447
C	-1.416212	2.687580	-1.742634
H	-1.207716	2.558712	-0.676097
H	-0.669619	3.356621	-2.184715
C	-2.821664	3.207429	-1.946156
H	-3.540263	2.538820	-1.466231
H	-3.054583	3.286844	-3.011805
H	-2.916120	4.197845	-1.490248
O	1.252463	1.117806	-2.858768

SCF energy: -1760.514840
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 1-Product-O5

C	-2.864296	-1.184109	-0.304806
H	-3.135791	-0.452203	0.459544
C	-0.472528	-1.267692	0.442294
H	0.566169	-1.186650	0.107462
C	-1.412915	-0.934034	-0.714920
O	-0.736353	-0.322130	1.489202
O	-1.278607	0.421487	-1.083470
C	-3.002862	-2.592704	0.291957
H	-3.996157	-2.719577	0.740715
C	-0.741491	-2.672782	0.953205
O	-2.096065	-2.846568	1.328584
B	-0.249855	0.852610	-1.851190
O	0.635889	-0.079518	-2.362202
C	-0.043521	2.339870	-2.192861
C	0.595937	4.967135	-2.899762
C	-0.792729	3.405618	-1.684194
C	1.028836	2.607077	-3.055430
C	1.347404	3.922836	-3.414598
C	-0.473128	4.710266	-2.032626
H	-1.616879	3.200443	-1.007889
H	2.181867	4.120584	-4.082459
H	-1.050827	5.537840	-1.632140
H	0.838667	5.991096	-3.167655
N	1.686090	0.240304	-3.214066
C	1.824259	1.481003	-3.519263
H	2.661177	1.660304	-4.191193
H	-0.454758	-3.396426	0.178028
O	-2.842757	-3.479651	-0.787657
C	-3.162566	-4.820946	-0.476822
H	-2.506137	-5.212707	0.308075
H	-3.025802	-5.399661	-1.391709
H	-4.206020	-4.907207	-0.143486
H	-1.156863	-1.587817	-1.557704
H	-0.148971	-2.866154	1.849425
O	-3.762131	-1.022865	-1.372458
H	-3.663676	-1.814482	-1.920988

P	0.436550	0.494219	2.191342
O	1.493013	-0.620339	2.680594
O	1.219035	1.109375	0.941630
C	2.429591	1.850237	1.195379
H	3.202058	1.143843	1.515905
H	2.242964	2.562196	2.005836
C	1.274276	-1.230764	3.964859
H	0.260461	-1.647774	4.000151
H	1.352008	-0.461608	4.738524
C	2.314965	-2.315304	4.142495
H	3.322359	-1.893119	4.086776
H	2.217034	-3.078616	3.364424
H	2.191319	-2.795550	5.118050
C	2.823908	2.561507	-0.079119
H	2.970424	1.840427	-0.888663
H	3.761957	3.103555	0.077666
H	2.051956	3.274641	-0.380123
O	-0.036488	1.410483	3.237332

SCF energy: -1760.510797
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

Epimer 2-Product-O4

C	2.713871	-0.357492	0.312155
C	1.510856	1.822752	0.849385
C	1.725690	0.693220	-0.173017
O	0.688265	1.317596	1.888913
O	0.445212	0.059688	-0.339553
C	3.989854	0.350507	0.788649
H	4.687880	-0.383599	1.209473
C	2.841312	2.298152	1.416422
O	3.679681	1.233455	1.826985
B	-0.642462	1.149231	1.623544
C	-1.469347	-0.010874	2.214137
C	-3.121813	-2.128724	2.987745
C	-2.792260	-0.088100	1.755608
C	-0.980336	-1.011513	3.060504
C	-1.799787	-2.063553	3.444848
C	-3.622684	-1.146046	2.148651
H	0.048795	-0.960192	3.403783
H	-1.418289	-2.841486	4.099416
H	-4.648551	-1.196272	1.792285
H	-3.757510	-2.954981	3.291851
O	-1.281810	2.074589	0.818251
N	-2.595696	1.953252	0.397533
C	-3.257594	0.946381	0.844056
H	-4.278713	0.907757	0.470732
H	2.655079	2.900599	2.307022
H	2.077327	1.111545	-1.121581
O	4.588103	1.053628	-0.267036
C	5.657647	0.388199	-0.905862
H	5.319317	-0.529072	-1.396329
H	6.453972	0.145335	-0.187245
H	6.054583	1.081572	-1.650563
O	3.061620	-1.287120	-0.681701
H	2.355439	-1.353824	-1.349770
H	3.352810	2.914583	0.667937
H	1.010026	2.661977	0.353969
H	2.264869	-0.858654	1.182607
P	-0.137933	-0.354341	-1.764067
O	0.822340	-1.140934	-2.572109
O	-1.497372	-1.074710	-1.362157
O	-0.631713	1.032076	-2.341724
C	-1.628207	1.146864	-3.376193
H	-2.393881	0.381432	-3.218915
H	-1.142771	0.973464	-4.341600
C	-1.453247	-2.359704	-0.705507
H	-0.663439	-2.966384	-1.159773
H	-1.214487	-2.189679	0.348887
C	-2.810105	-3.006968	-0.867669
H	-3.589524	-2.359597	-0.456398
H	-2.831946	-3.958309	-0.327426
H	-3.026832	-3.195977	-1.922828
C	-2.218842	2.536174	-3.272860
H	-2.654723	2.681904	-2.280313
H	-2.995995	2.667605	-4.032709
H	-1.446679	3.294568	-3.430443

SCF energy: -1760.508304
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

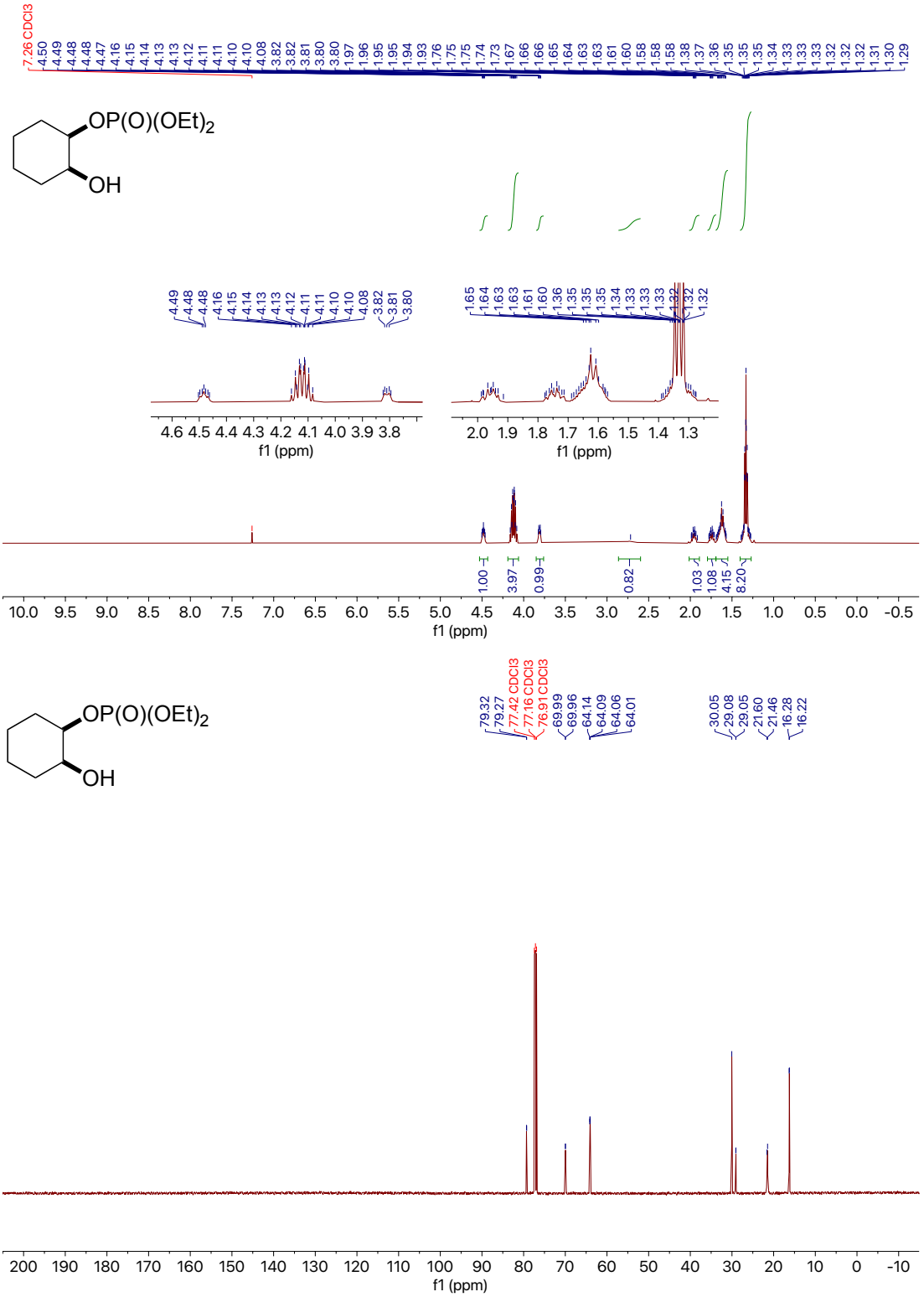
Epimer 2-Product-O5

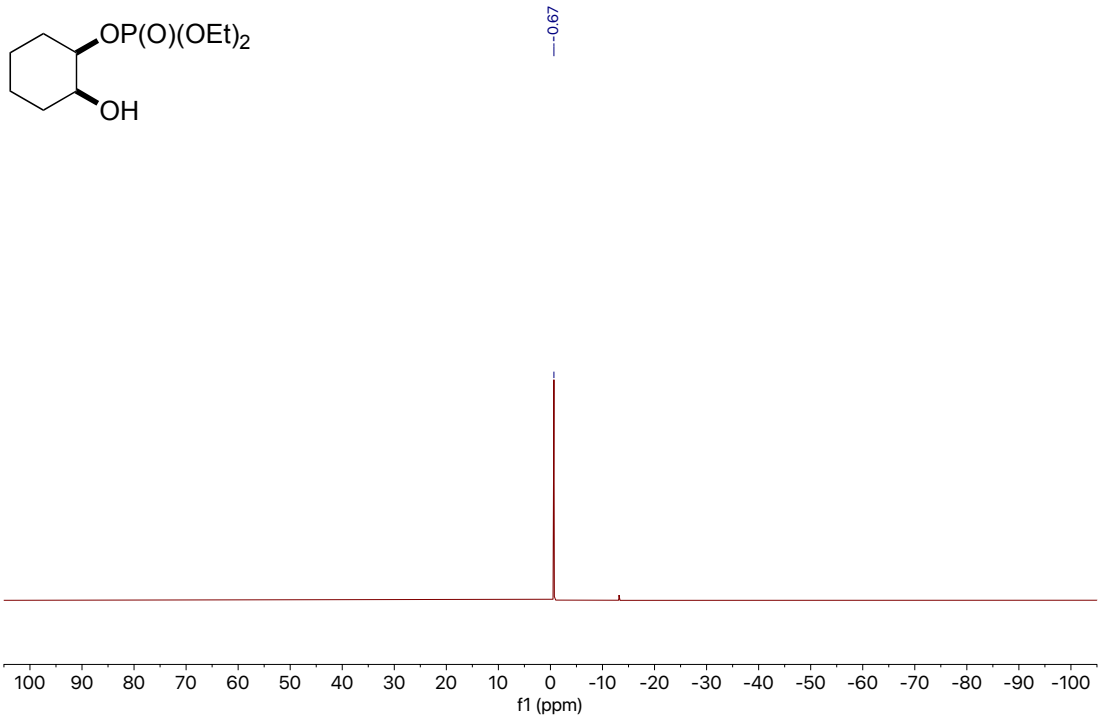
C	-0.953406	-0.118436	2.349949
C	-1.517621	0.317504	-0.026925
C	-0.941174	0.941277	1.242460
O	-0.584656	-0.705398	-0.393644
O	0.313569	1.521968	0.928863
C	-2.401344	-0.602246	2.534855
H	-2.419751	-1.408991	3.277128
C	-2.904895	-0.244109	0.264644
O	-2.883566	-1.161260	1.342859
B	1.567618	1.042272	1.090778
C	2.743066	1.591912	0.253349
C	4.998977	2.337910	-1.225062
C	3.968889	0.936603	0.437483
C	2.668461	2.643151	-0.667328
C	3.786307	3.014543	-1.400478
C	5.097196	1.305167	-0.306754
H	1.725329	3.165206	-0.802213
H	3.724258	3.830958	-2.113985
H	6.040313	0.785225	-0.161651
H	5.868242	2.627709	-1.807423
O	1.843021	0.062446	2.032358
N	3.091630	-0.533868	2.204271
C	4.033792	-0.117053	1.438814
H	4.976735	-0.630263	1.614094
H	-3.286268	-0.788018	-0.599710
H	-1.587061	1.765340	1.559096
O	-3.245485	0.446298	2.924737
C	-3.474918	0.549915	4.315212
H	-4.211462	1.344828	4.449480
H	-2.557390	0.802532	4.854905
H	-3.887013	-0.387318	4.716449
O	-0.485659	0.385002	3.576805
H	0.476558	0.283343	3.552294
H	-3.584393	0.589739	0.481738
H	-1.581519	1.065761	-0.825340
H	-0.366443	-0.985006	2.031242
P	-0.450658	-1.349343	-1.862052
O	-0.542952	-0.116647	-2.872292
O	-1.866988	-2.007871	-2.192061
O	0.727373	-2.226915	-1.915802
C	0.494821	0.885156	-2.835889
H	0.693015	1.158676	-1.794377
H	0.055310	1.750924	-3.336956
C	-2.204550	-3.218713	-1.478169
H	-2.205292	-3.005016	-0.403082
H	-1.441402	-3.973460	-1.689284
C	1.765591	0.433331	-3.528995
H	1.558417	0.160399	-4.567555
H	2.201288	-0.429469	-3.020072
H	2.492149	1.252513	-3.515988
C	-3.573058	-3.660710	-1.946989
H	-4.326183	-2.899127	-1.723477
H	-3.856299	-4.585444	-1.435111
H	-3.570519	-3.842928	-3.025196

SCF energy: -1760.502676
ωB97X-D (Gas Phase) / 6-31G (d) opt.
No imaginary frequency

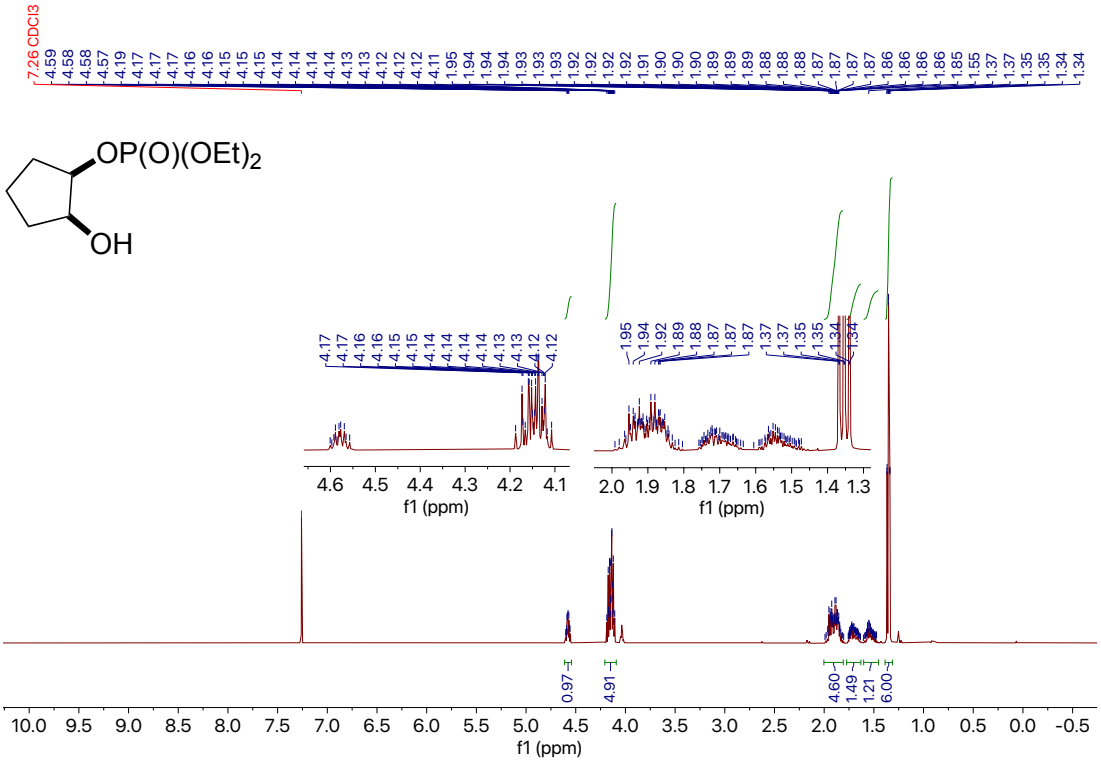
9. NMR Spectra

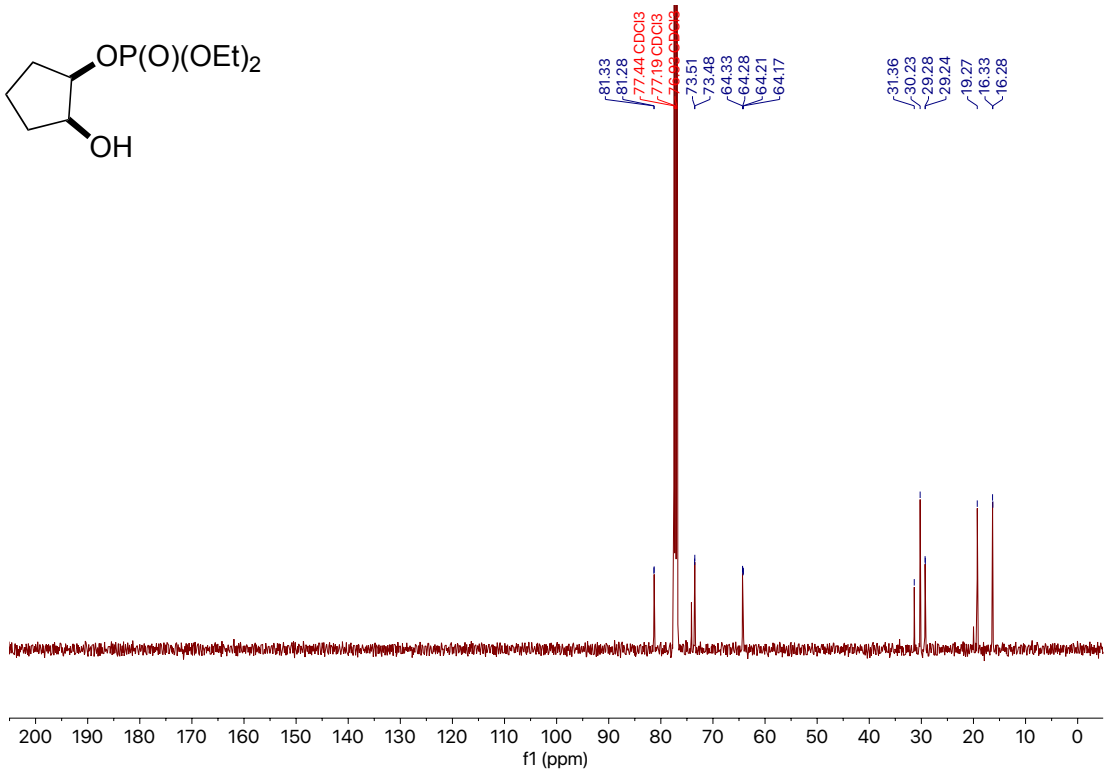
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for Diethyl (2-hydroxycyclohexyl) phosphate **(2a)** in $CDCl_3$

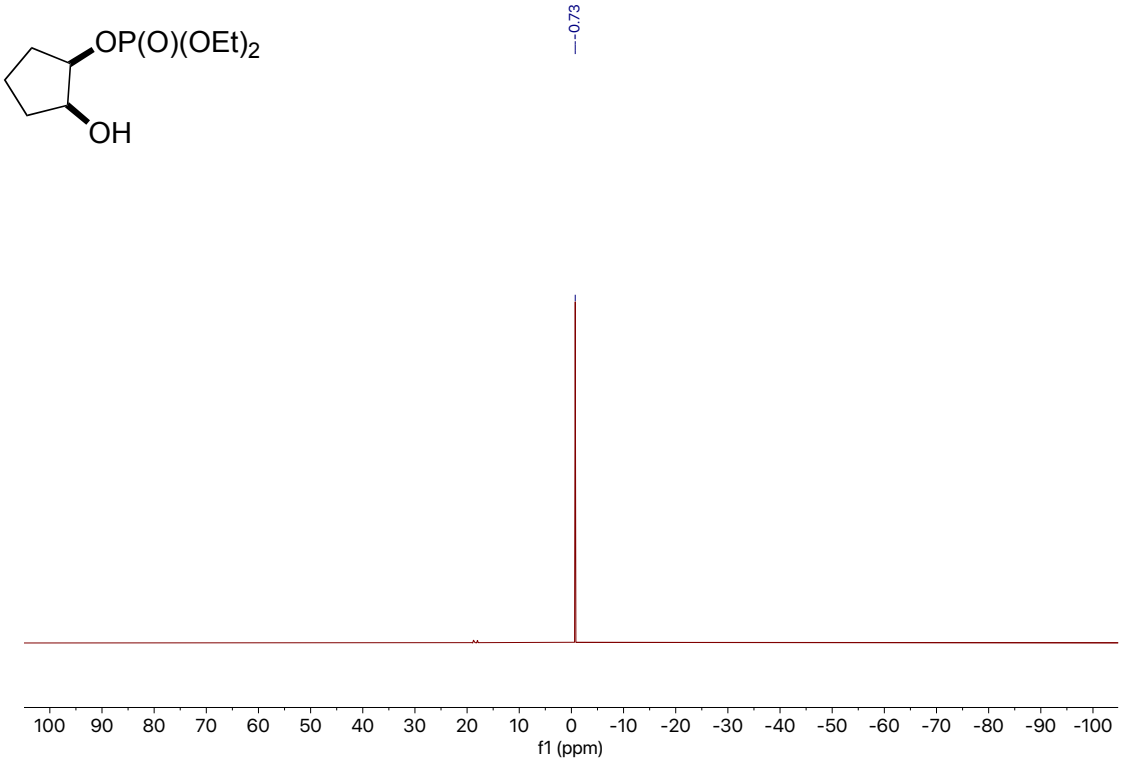




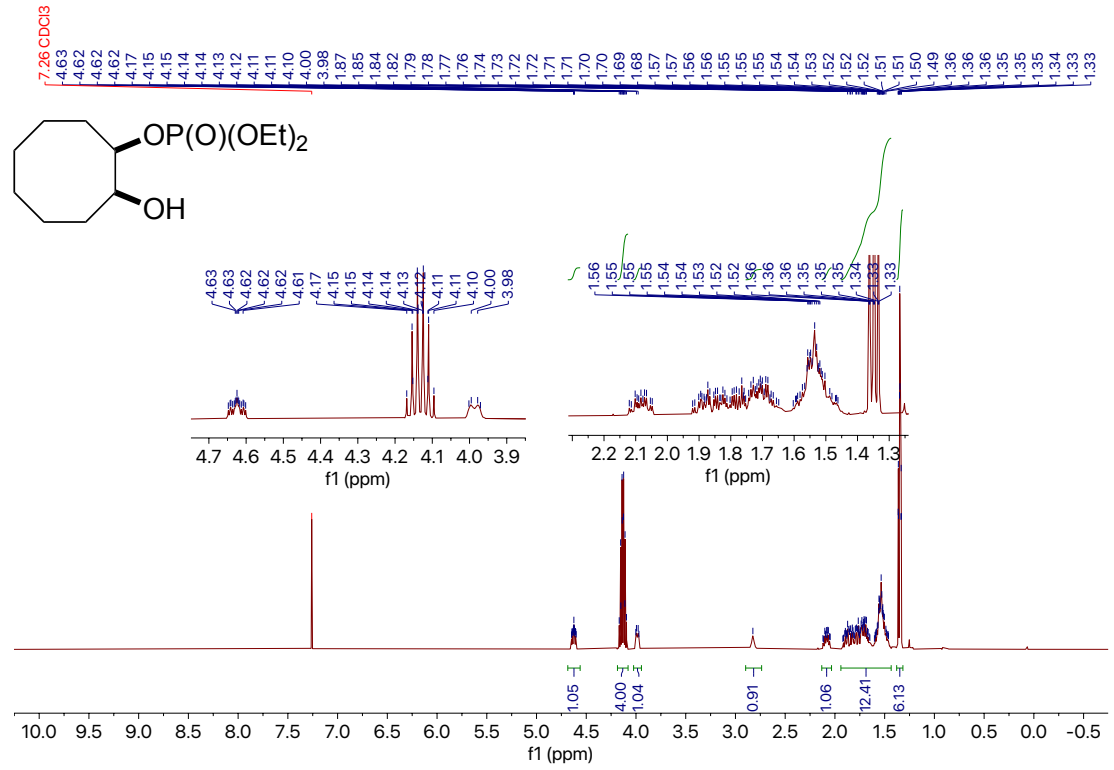
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for Diethyl (2-hydroxycyclopentyl) phosphate **(2b)** in $CDCl_3$

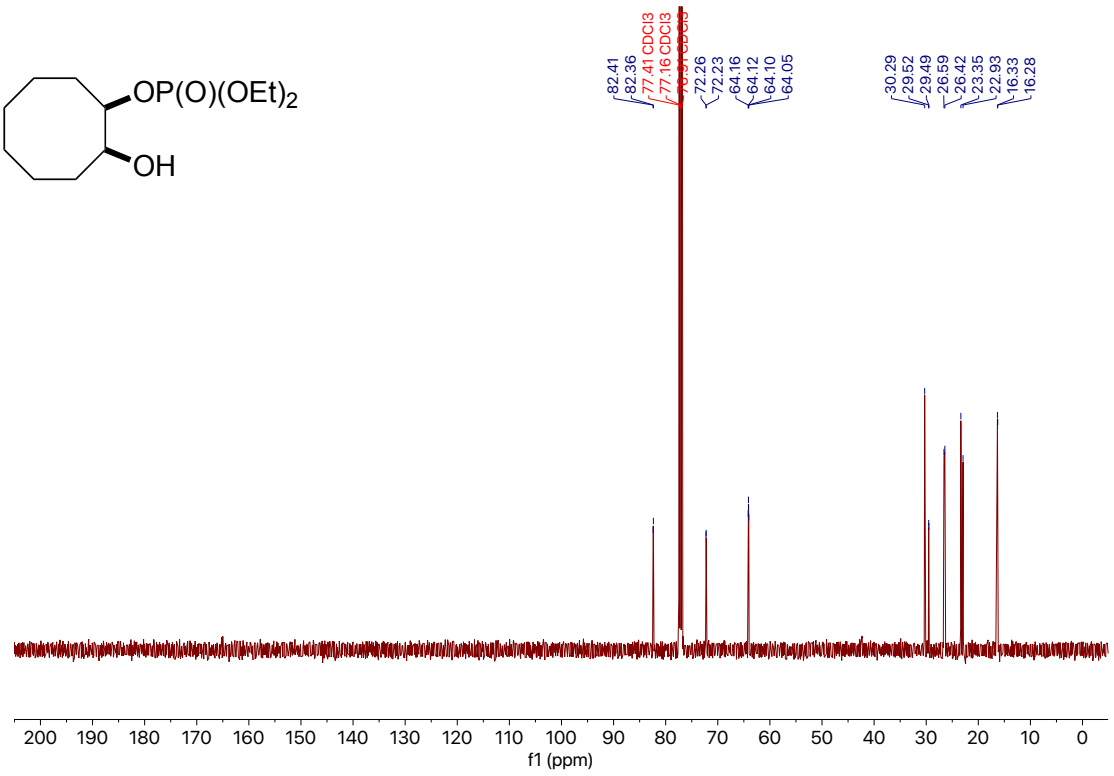


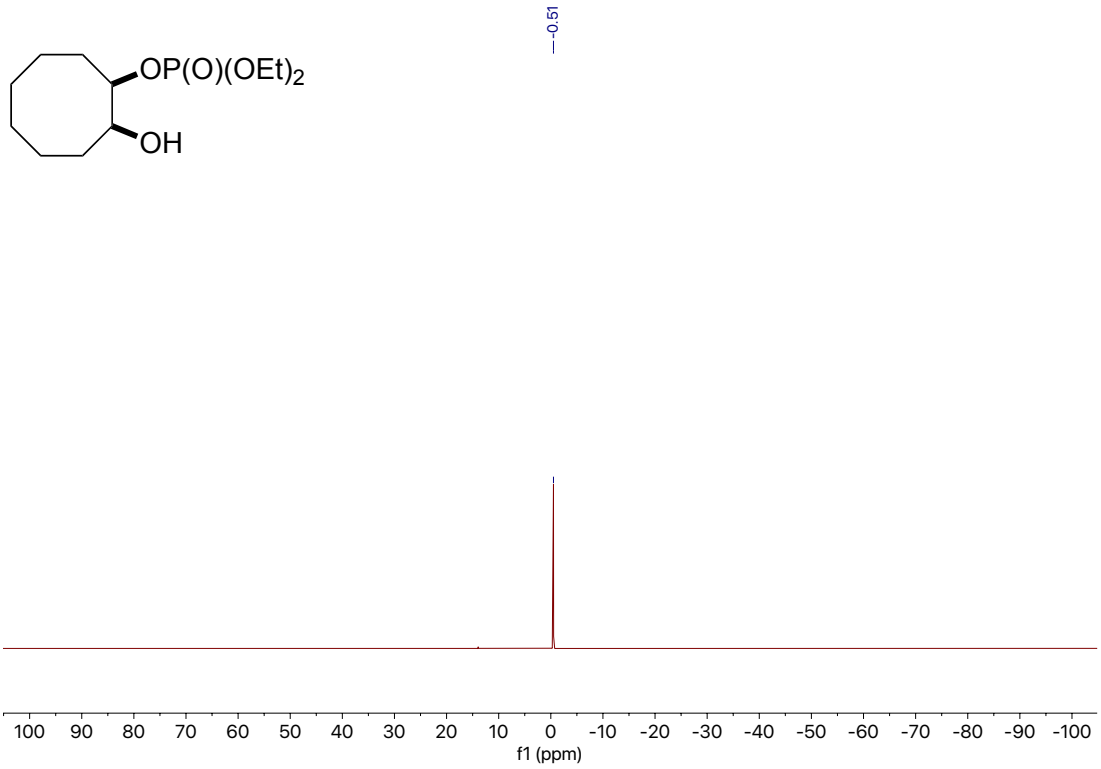

OP(O)(OEt)2
OH
81.33
81.28
77.44 CDCl3
77.19 CDCl3
73.51
73.48
64.33
64.28
64.21
64.17
31.36
30.23
29.28
29.24
19.27
16.33
16.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OP(O)(OEt)2
OH
0.73
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

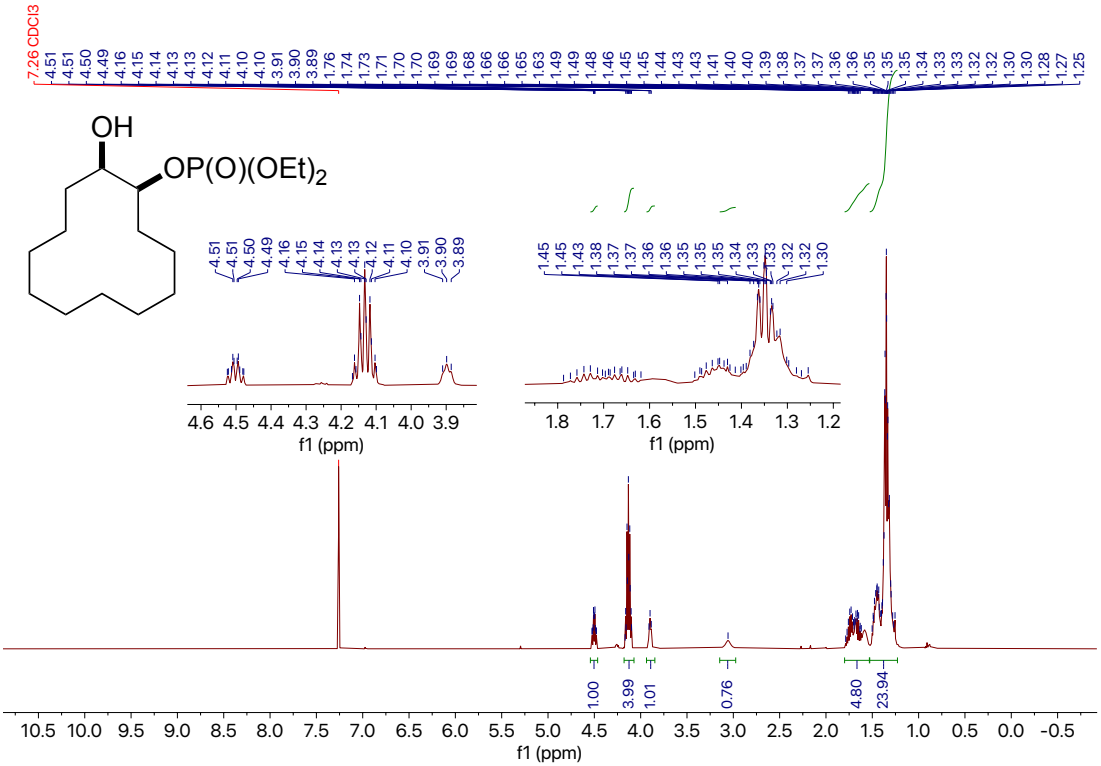
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for Diethyl (2-hydroxycyclooctyl) phosphate **(2c)** in $CDCl_3$

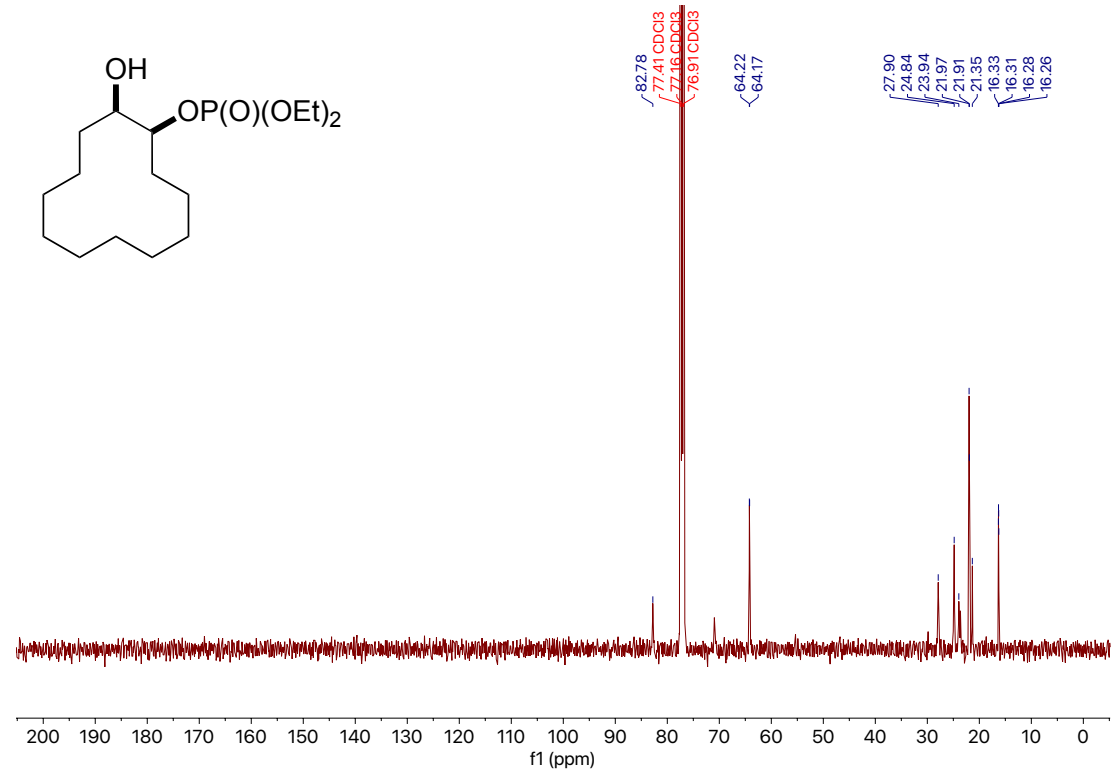


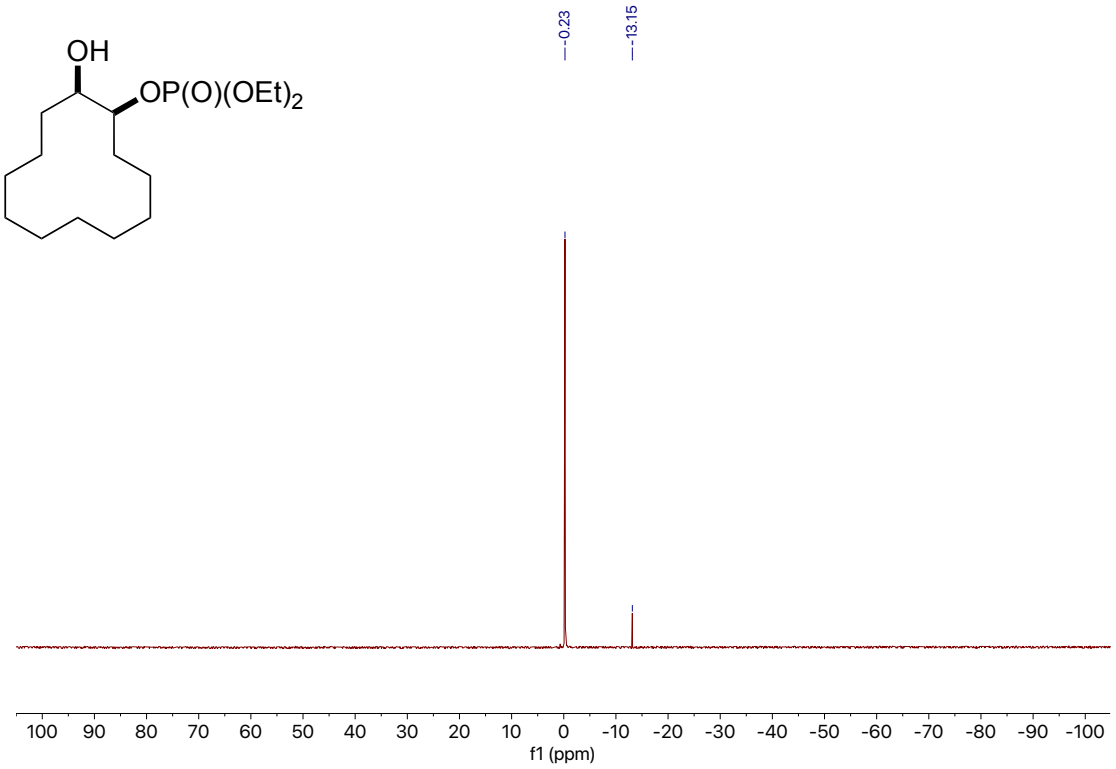




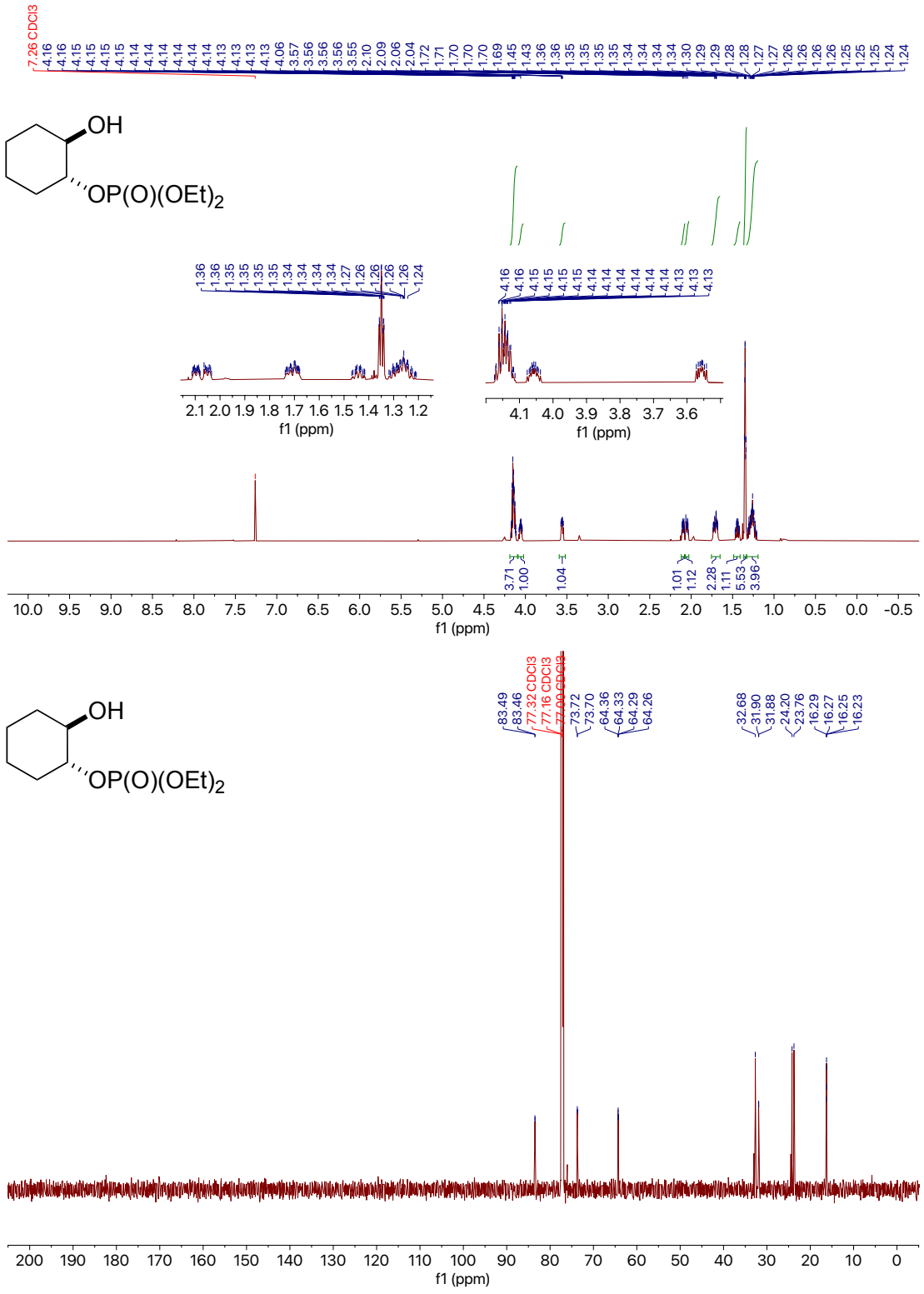
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for Diethyl (2-hydroxycyclododecyl) phosphate **(2d)** in $CDCl_3$

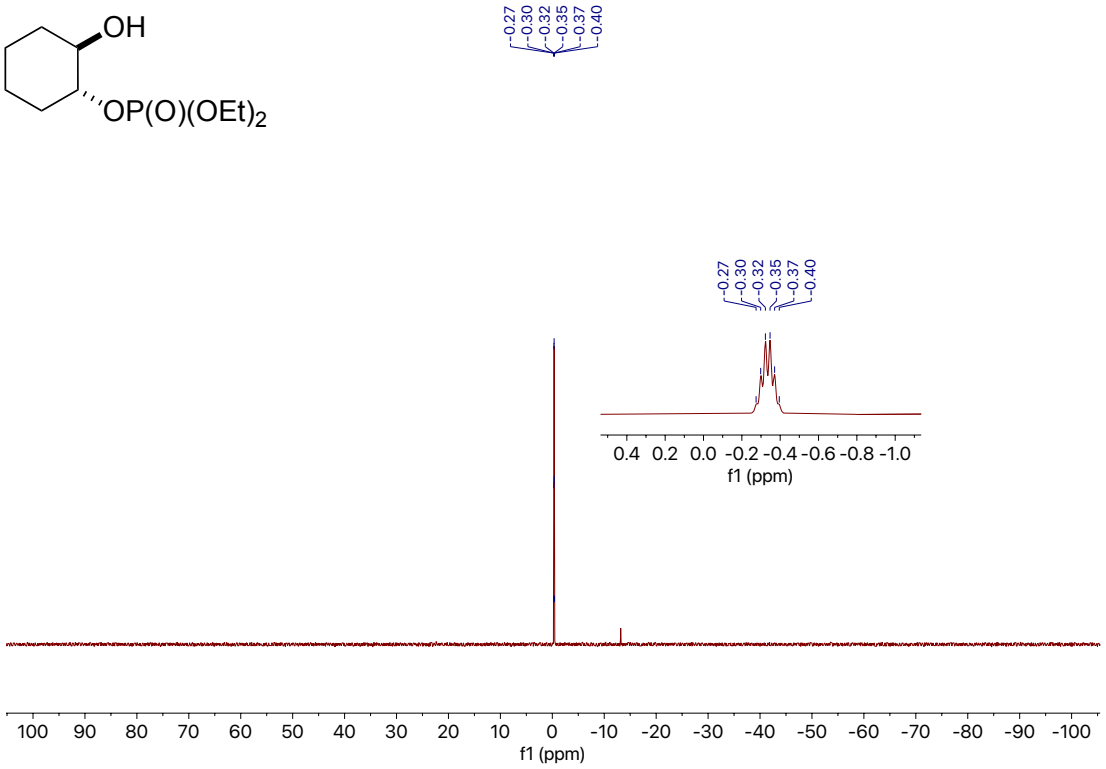



OH
OP(O)(OEt)2
82.78
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.22
64.17
27.90
24.84
23.94
21.97
21.91
21.35
16.33
16.31
16.28
16.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

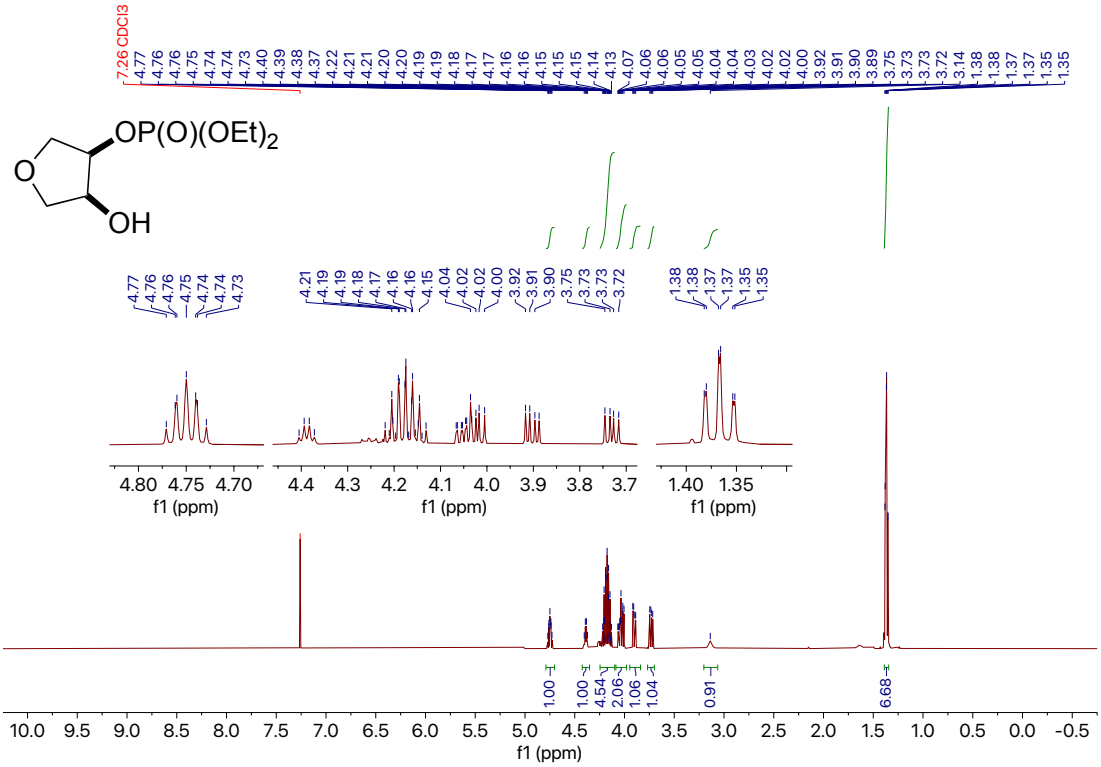

OH
OP(O)(OEt)2
0.23
13.15
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

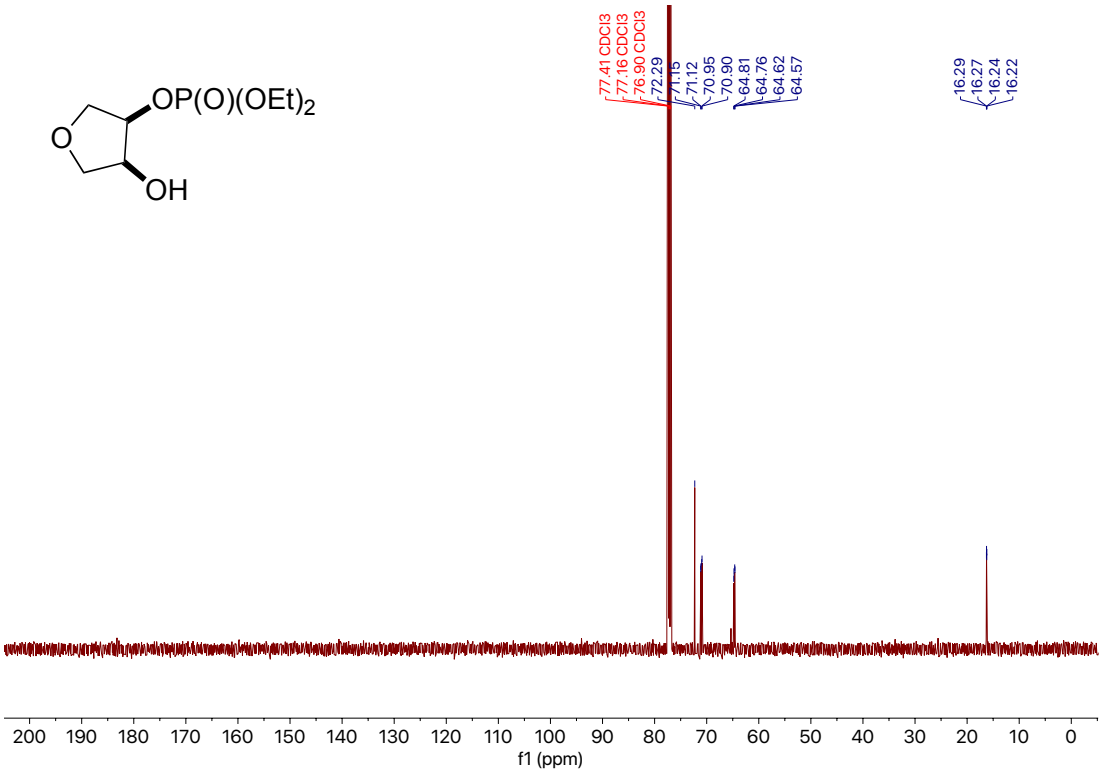
^{1}H, $^{13}C\{^{1}H\}$, and ^{31}P NMR for **Diethyl (*trans*–2-hydroxycyclohexyl) phosphate (2e)** in $CDCl_3$

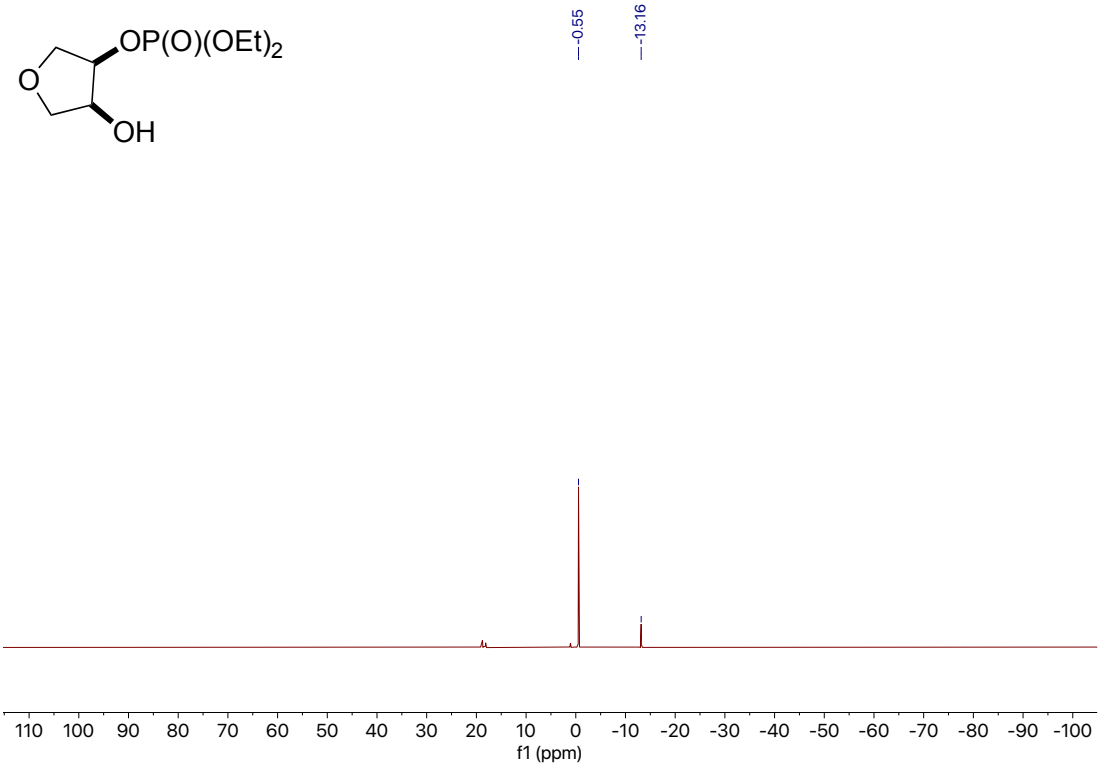




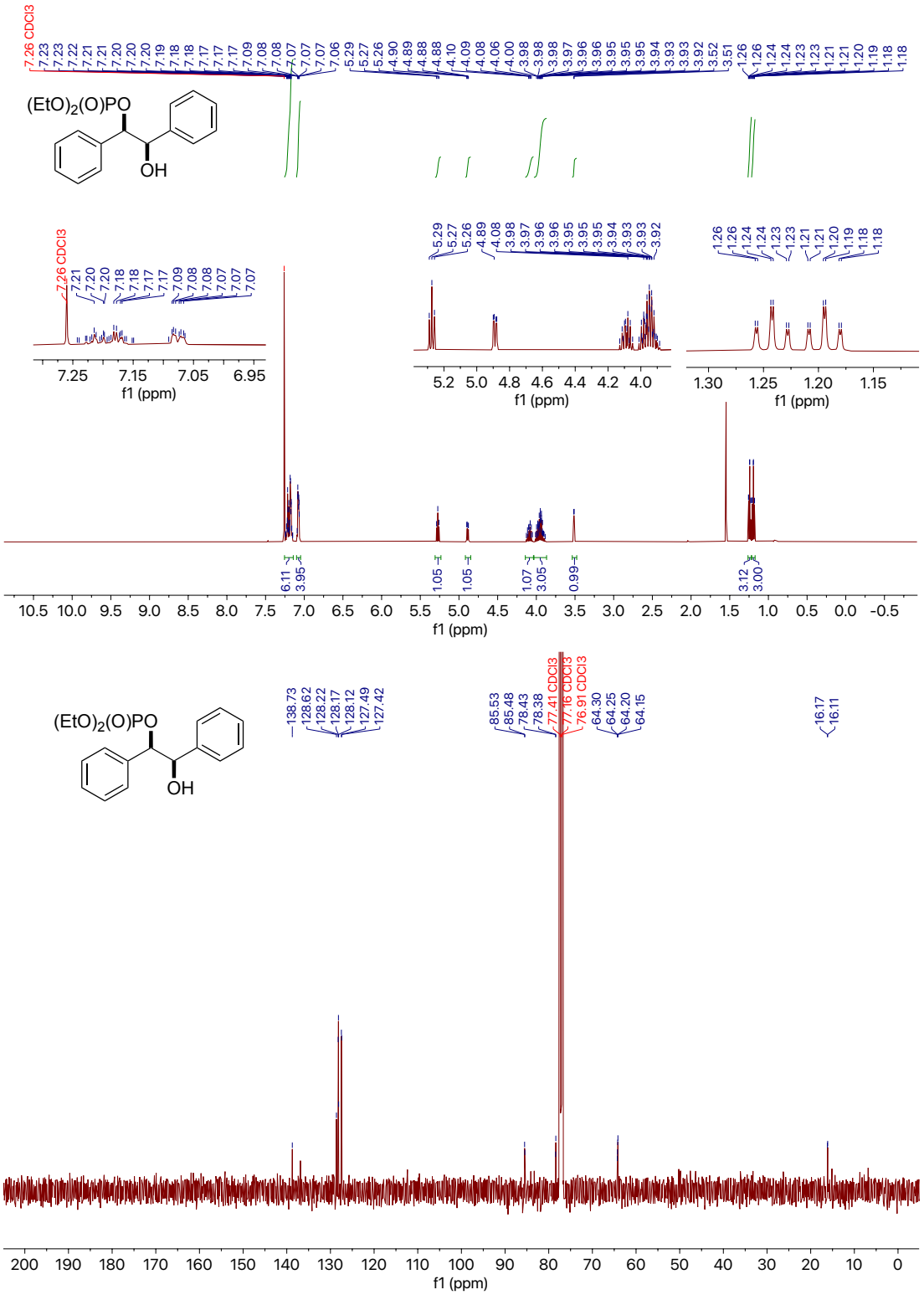
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for **Diethyl (4-hydroxytetrahydrofuran-3-yl) phosphate (2f)** in $CDCl_3$

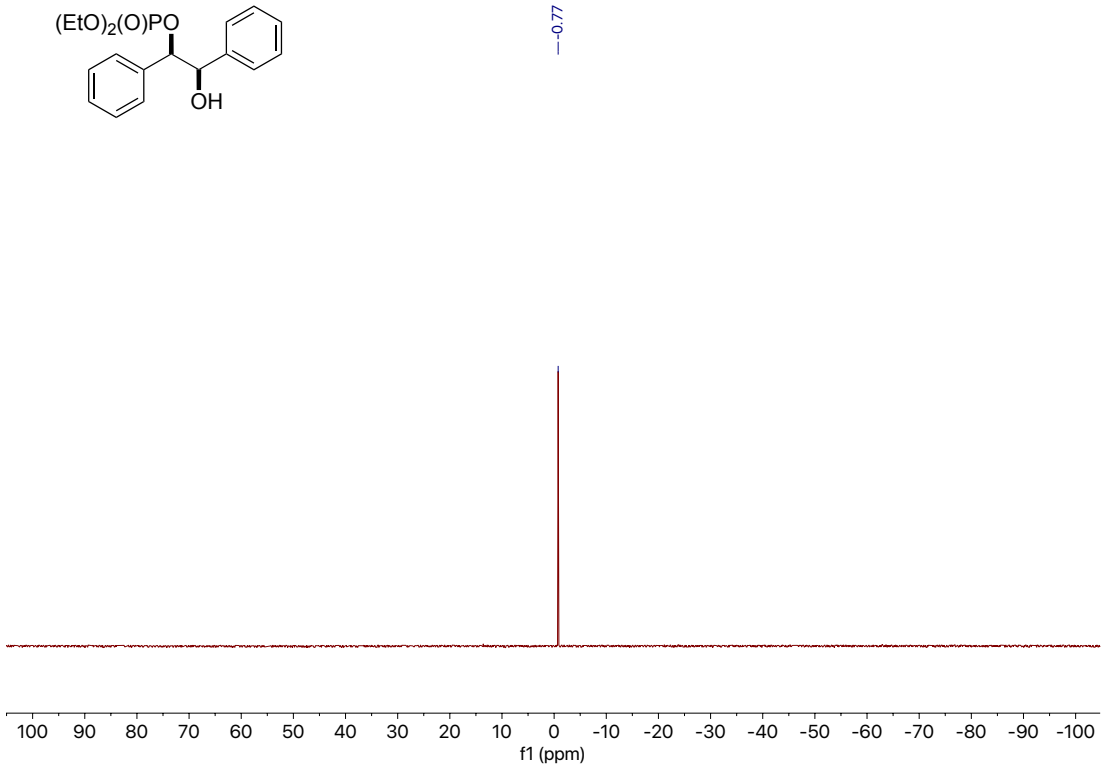



OP(O)(OEt)2
O
OH
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
72.29
71.15
71.12
70.95
70.90
64.81
64.76
64.62
64.57
16.29
16.27
16.24
16.22
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

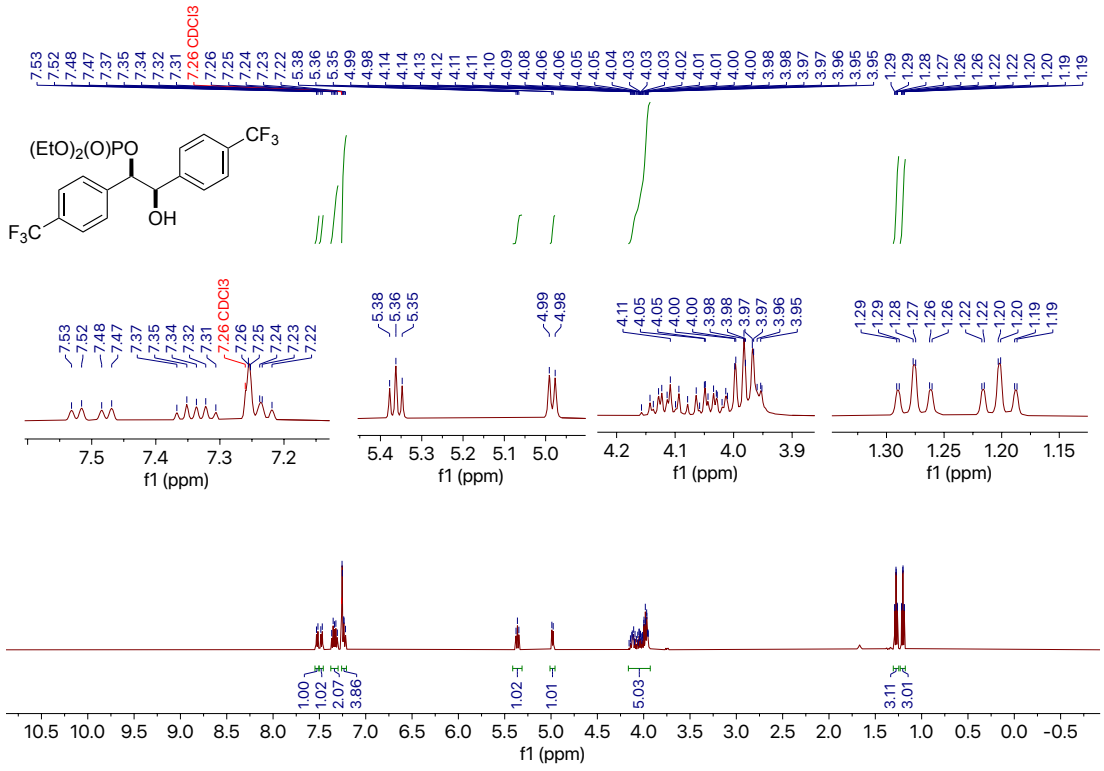

OP(O)(OEt)2
O
OH
-0.55
-13.16
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

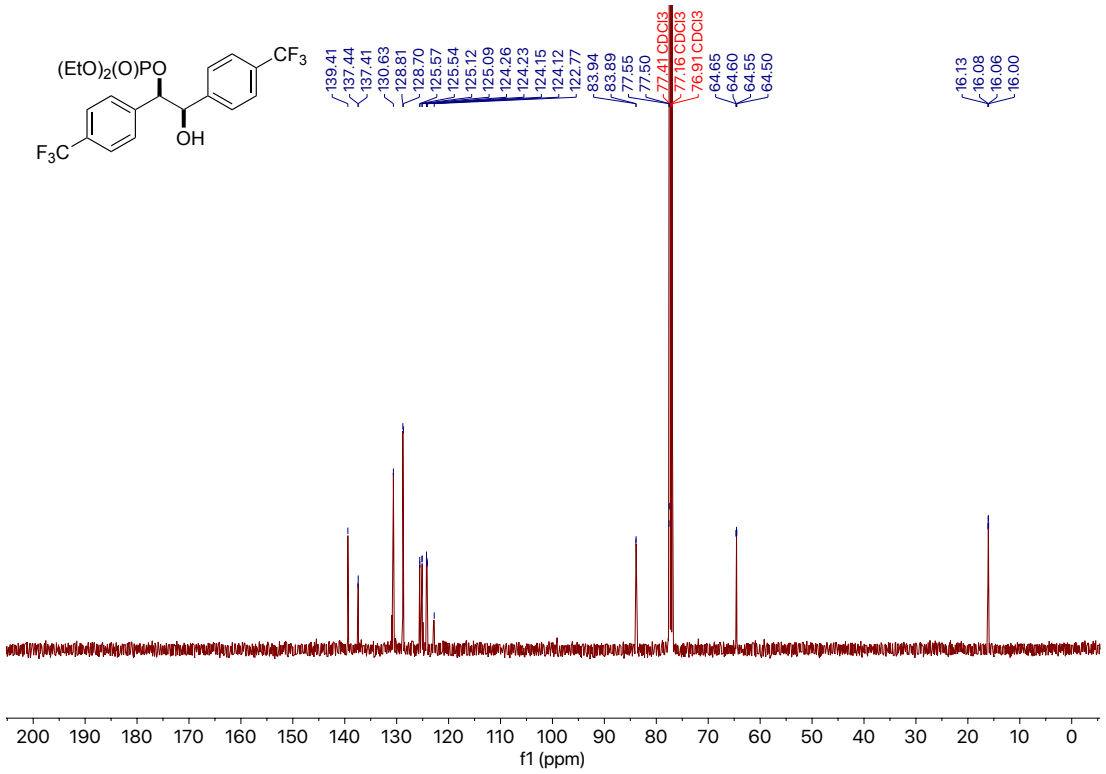
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{1H\}$ NMR for **Diethyl (2-hydroxy-1,2-diphenylethyl) phosphate (2g)** in $CDCl_3$

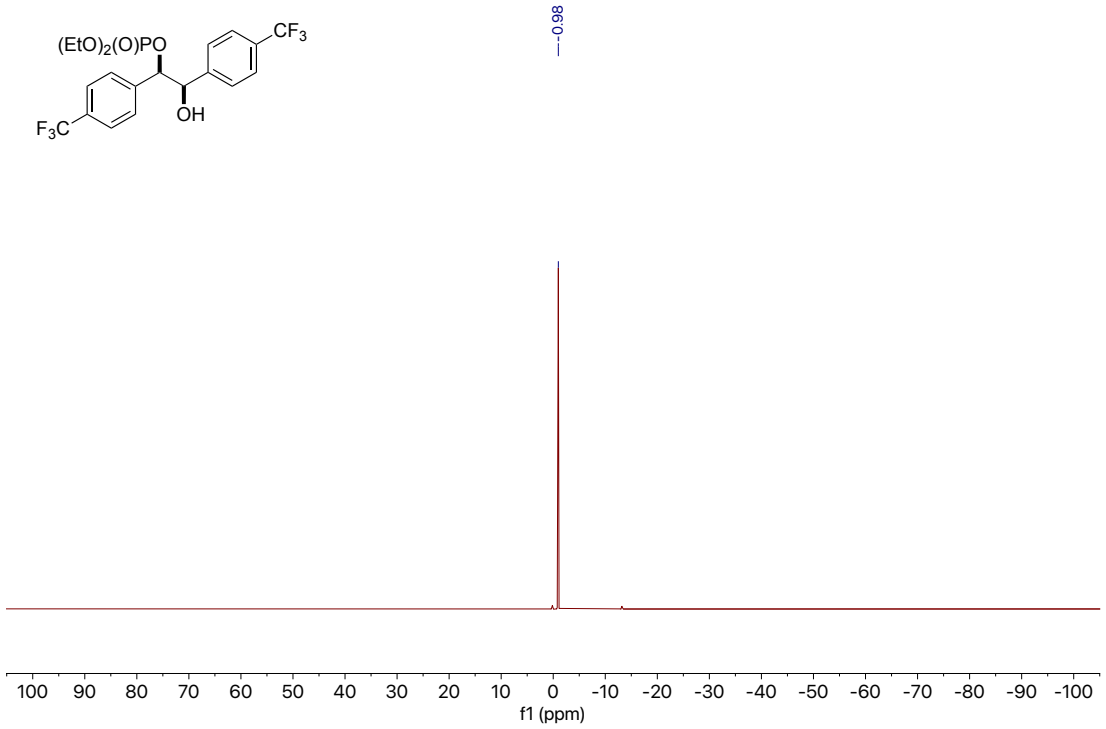


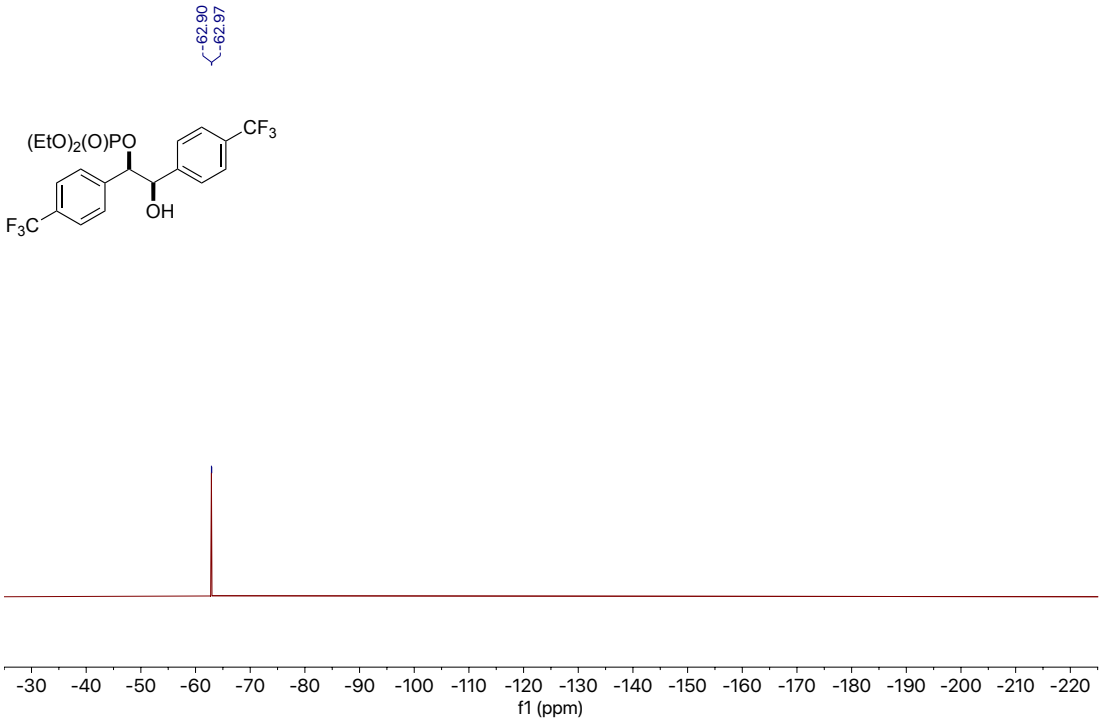


^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR for **Diethyl (2-hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)ethyl) phosphate (2h)** in $CDCl_3$

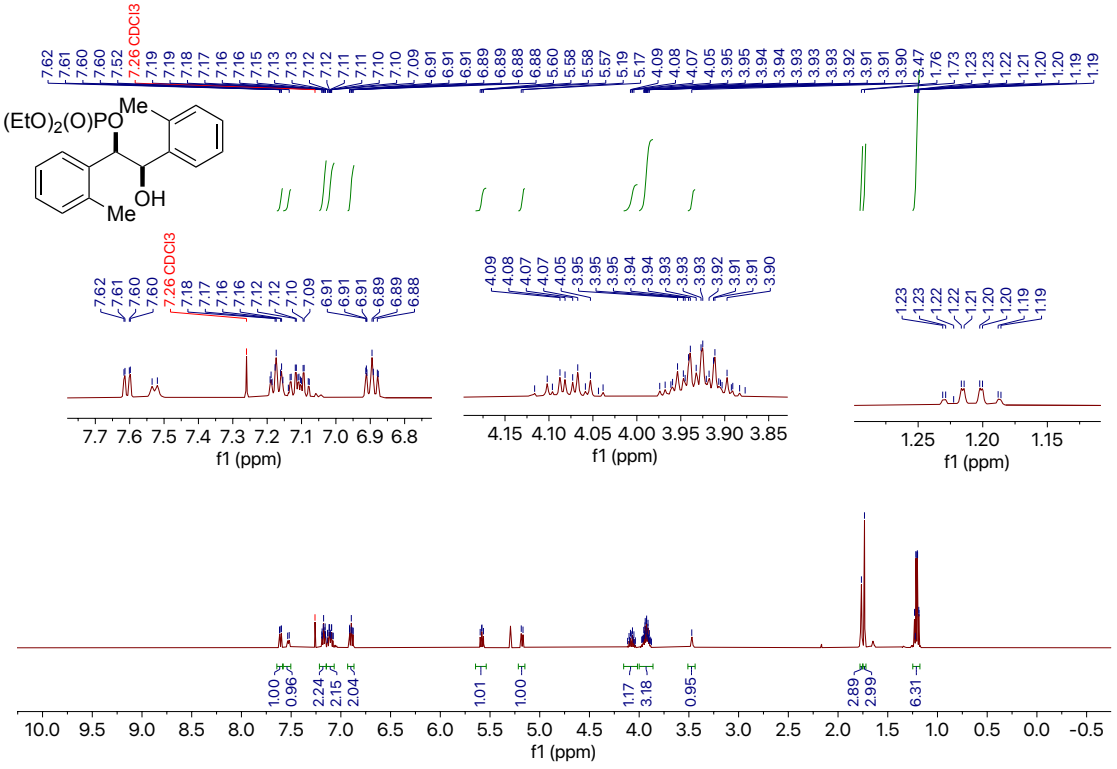


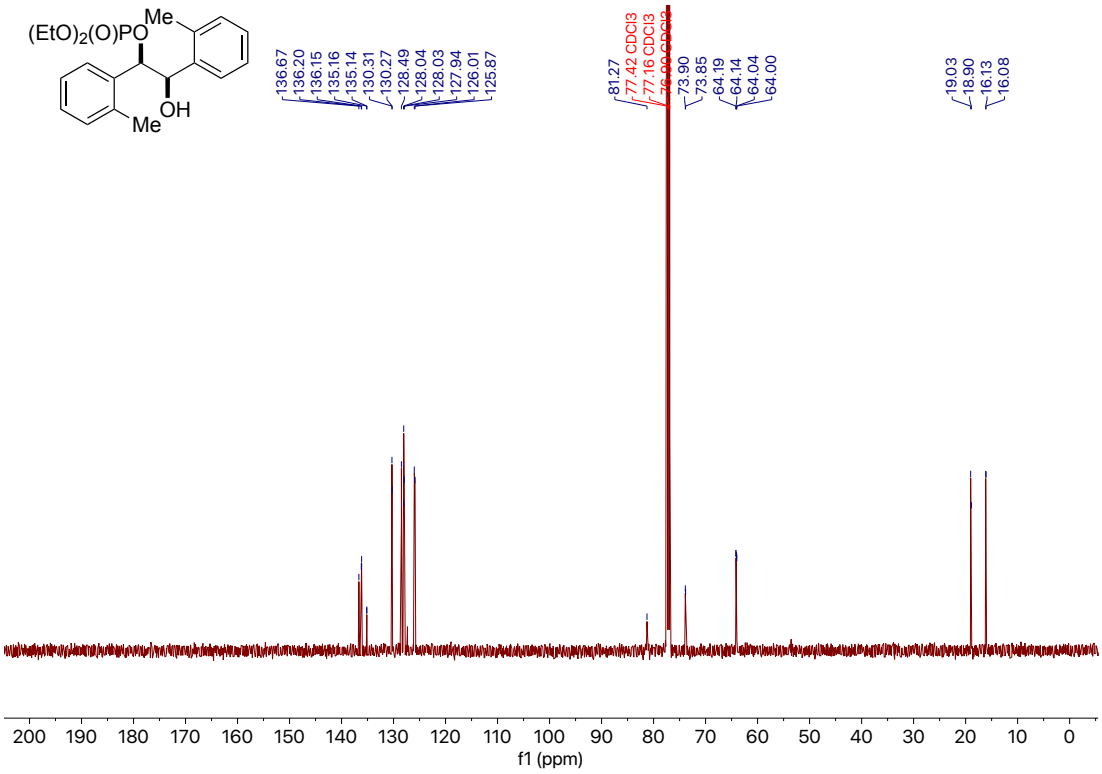

(EtO)2(O)PO
CF3
OH
F3C
139.41
137.44
137.41
130.63
128.81
128.70
125.57
125.54
125.12
125.09
124.26
124.23
124.15
124.12
122.77
83.94
83.89
77.55
77.50
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
64.65
64.60
64.55
64.50
16.13
16.08
16.06
16.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

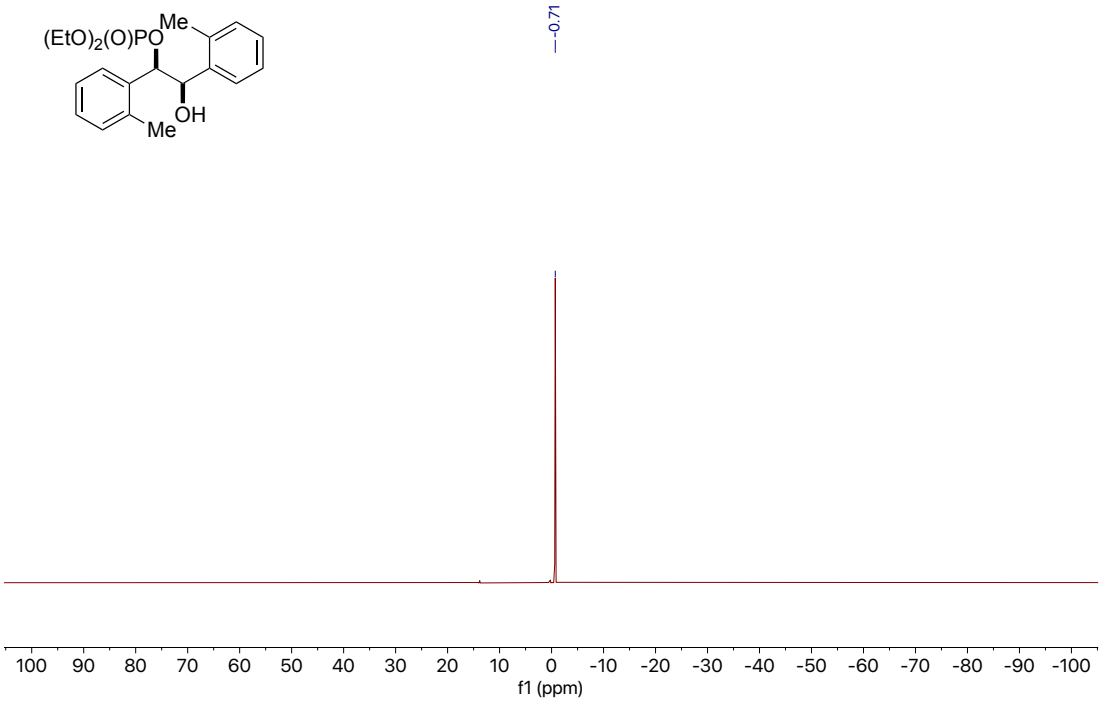

(EtO)2(O)PO
CF3
OH
F3C
-0.98
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)



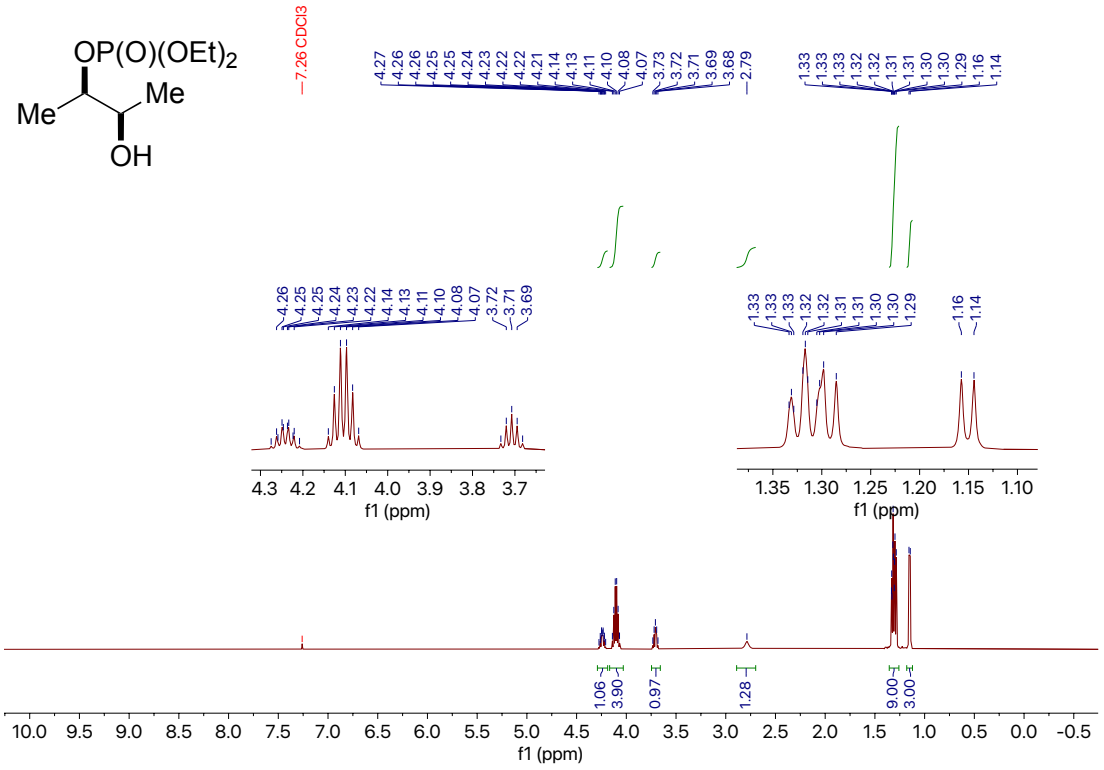
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Diethyl (2-hydroxy-1,2-bis(2-(methyl)phenyl)ethyl) phosphate (2i)** in $CDCl_3$

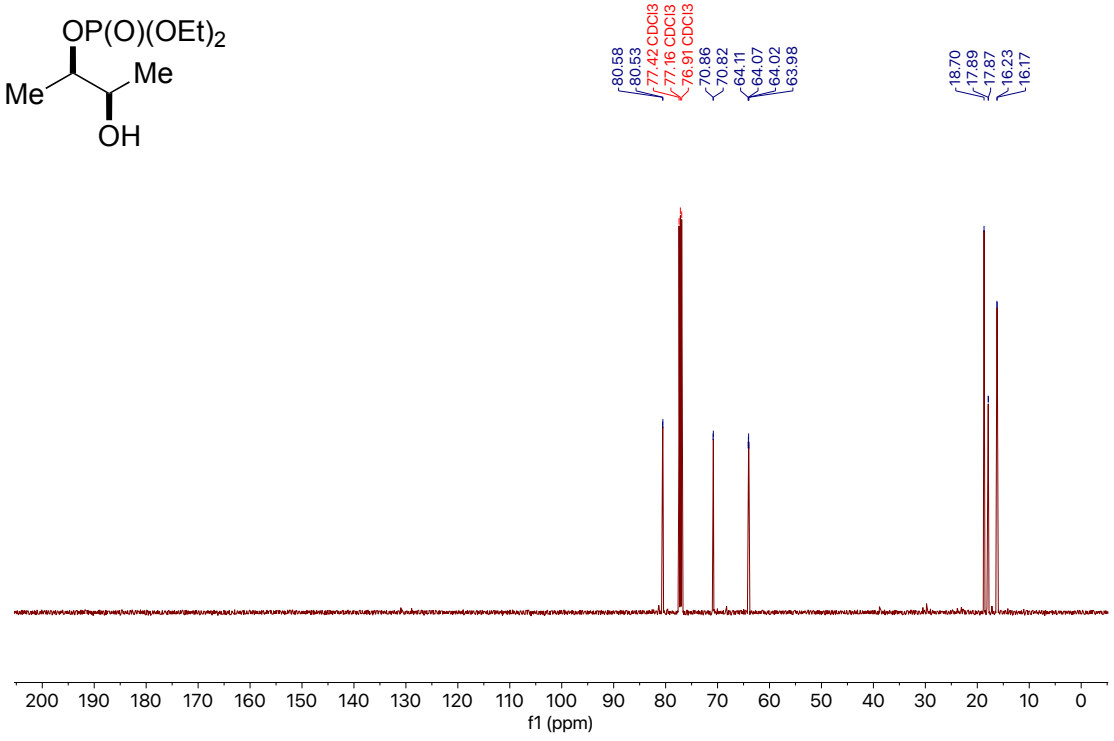


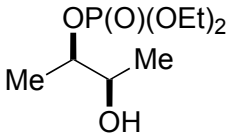

(EtO)2(O)PO
Me
OH
Me
136.67
136.20
136.15
135.16
135.14
130.31
130.27
128.49
128.04
128.03
127.94
126.01
125.87
81.27
77.42 CDCl3
77.16 CDCl3
76.90 CDCl3
73.90
73.85
64.19
64.14
64.04
64.00
19.03
18.90
16.13
16.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(EtO)2(O)PO
Me
OH
Me
-0.71
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

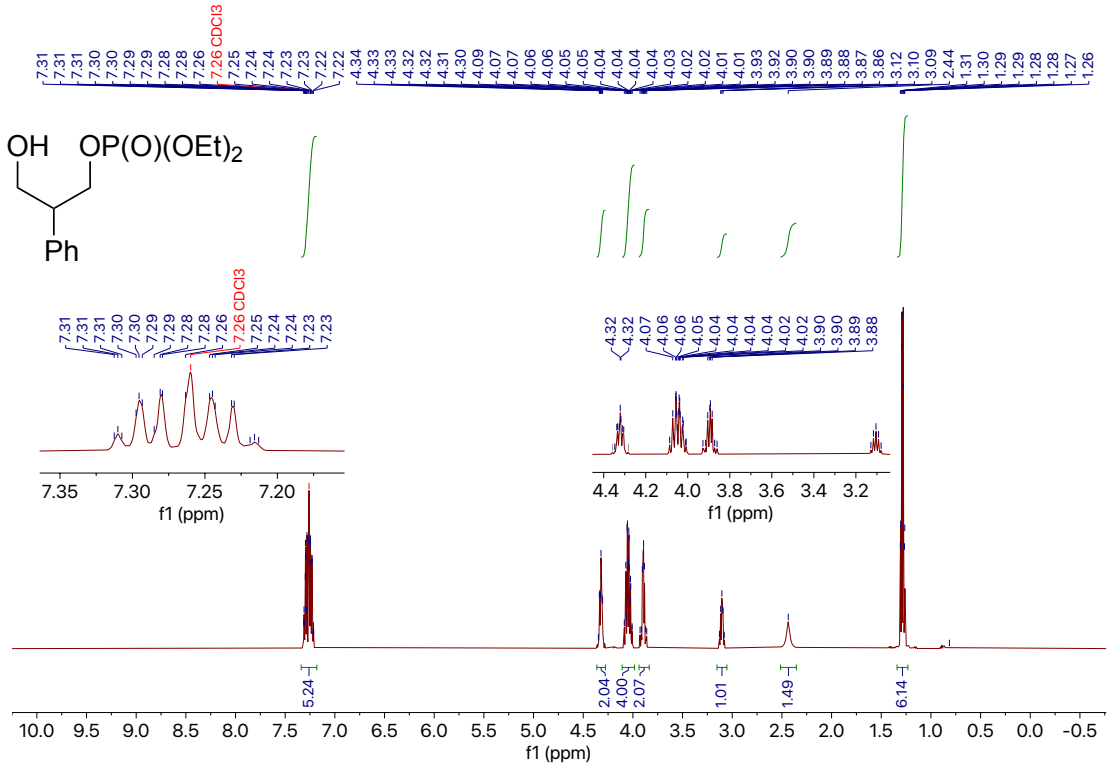
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Diethyl (3-hydroxybutan-2-yl) phosphate (2j)** in $CDCl_3$

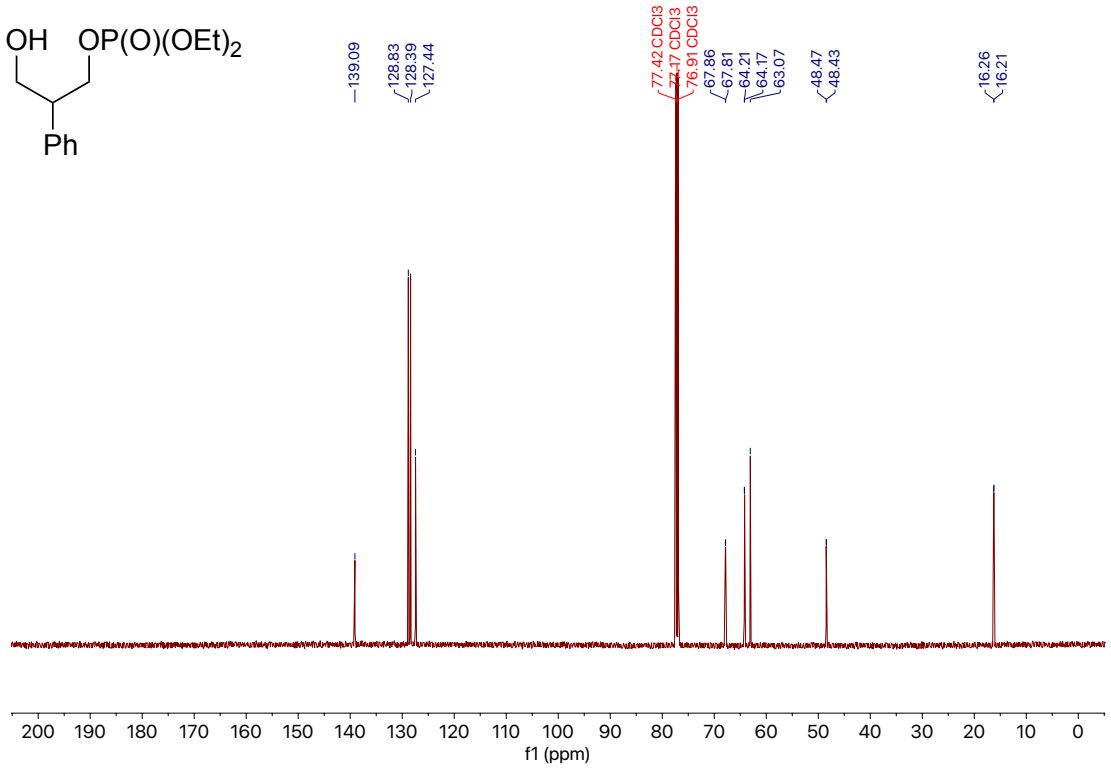


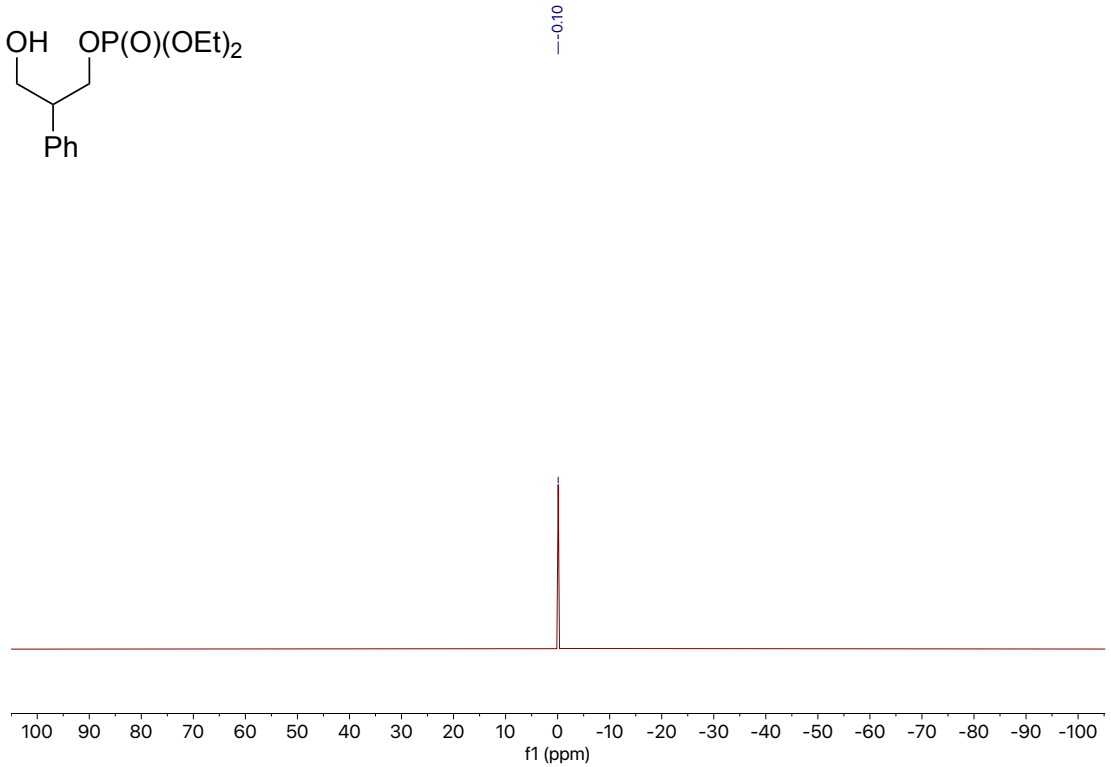




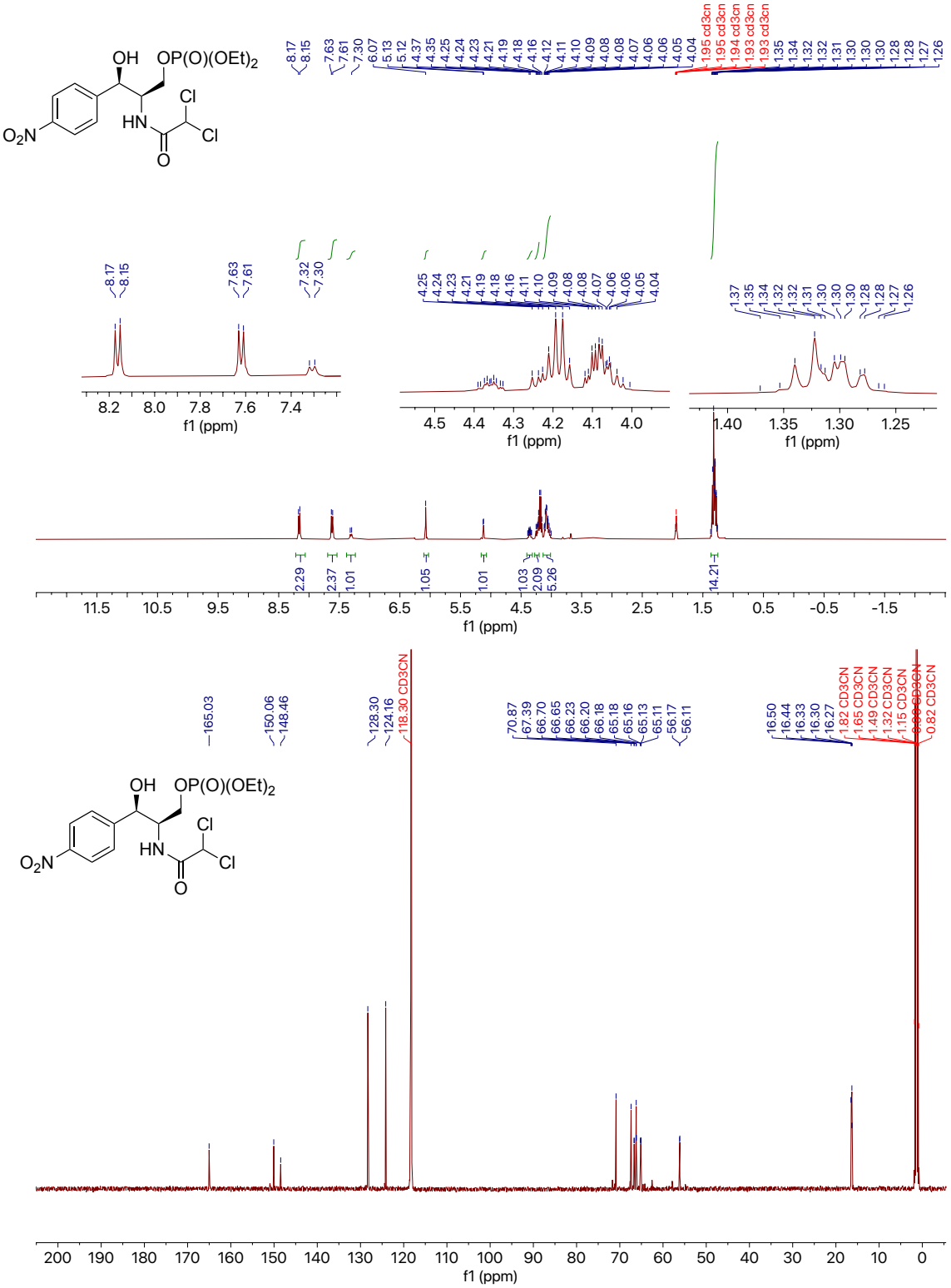
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Diethyl (3-hydroxy-2-phenylpropyl) phosphate (2k)** in $CDCl_3$

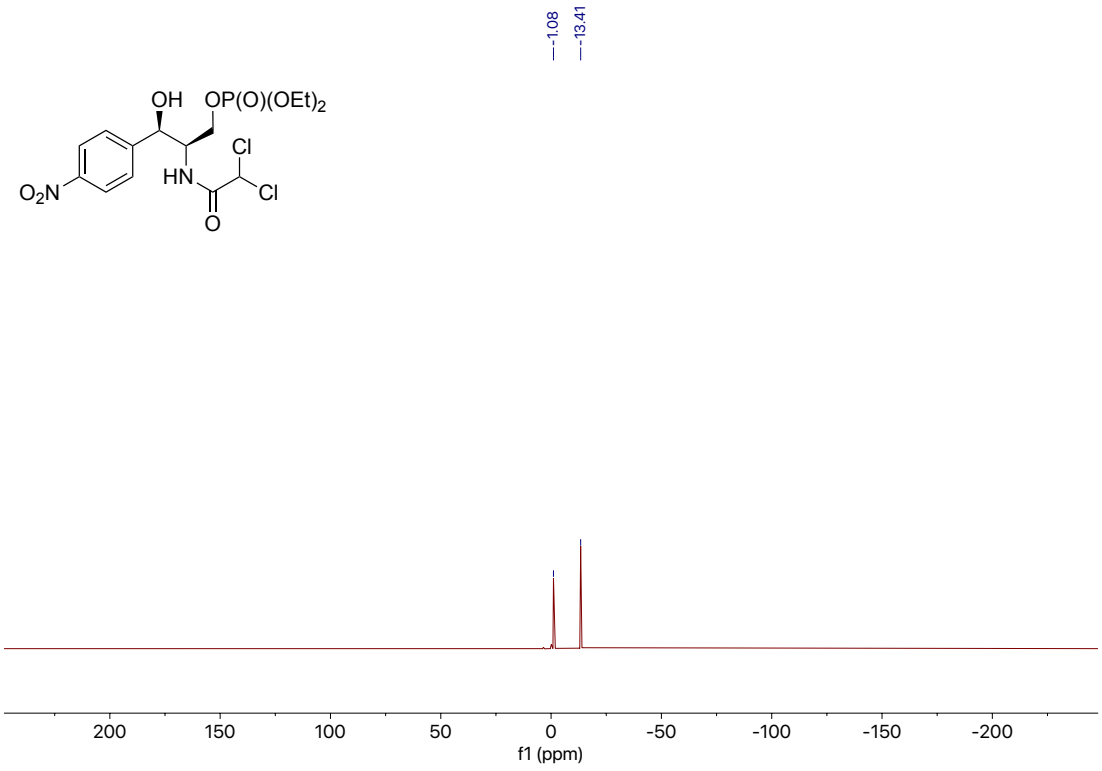



OH
OP(O)(OEt)2
Ph
139.09
128.83
128.39
127.44
77.42 CDCl3
77.17 CDCl3
76.91 CDCl3
67.86
67.81
64.21
64.17
63.07
48.47
48.43
16.26
16.21
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

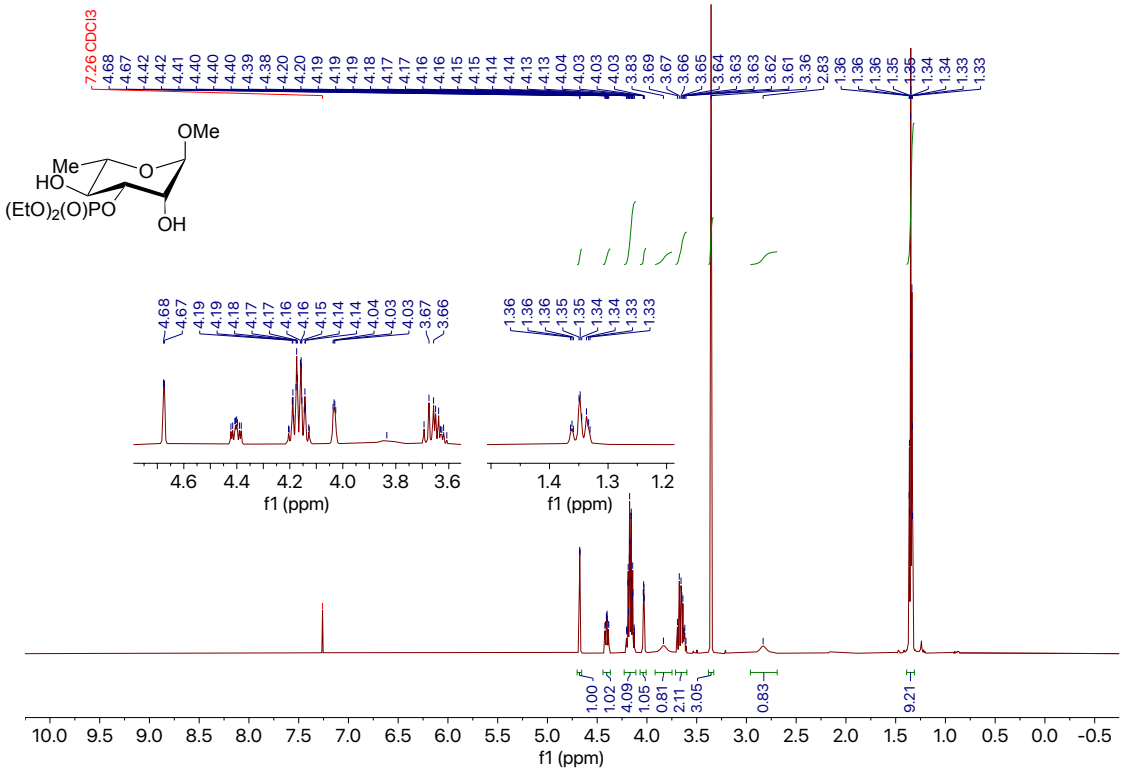

OH
OP(O)(OEt)2
Ph
0.10
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

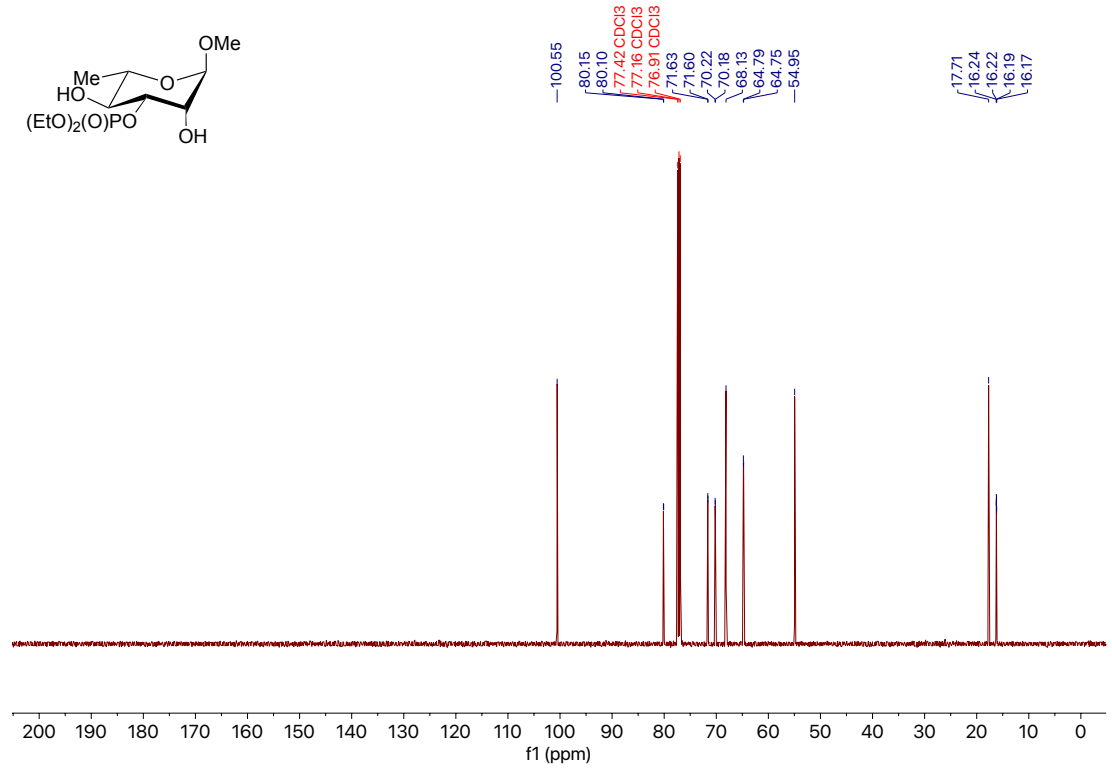
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*R*,3*R*)-2-(2,2-dichloroacetamido)-3-hydroxy-3-(4-nitrophenyl)propyl diethyl phosphate (2l)** in CD_3CN.

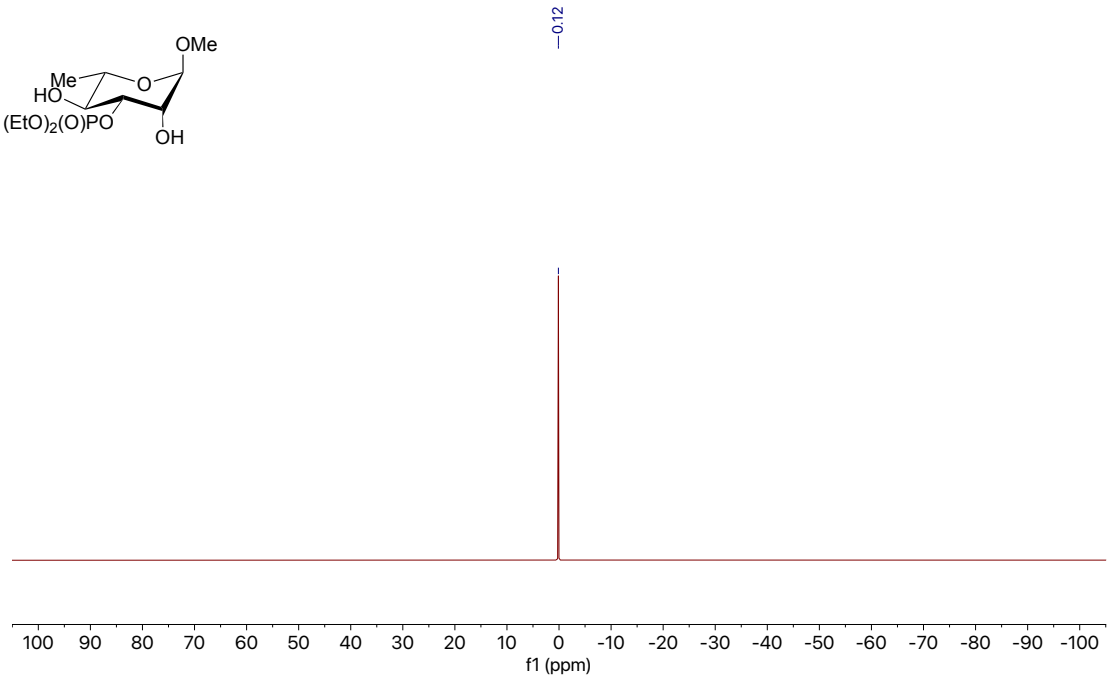




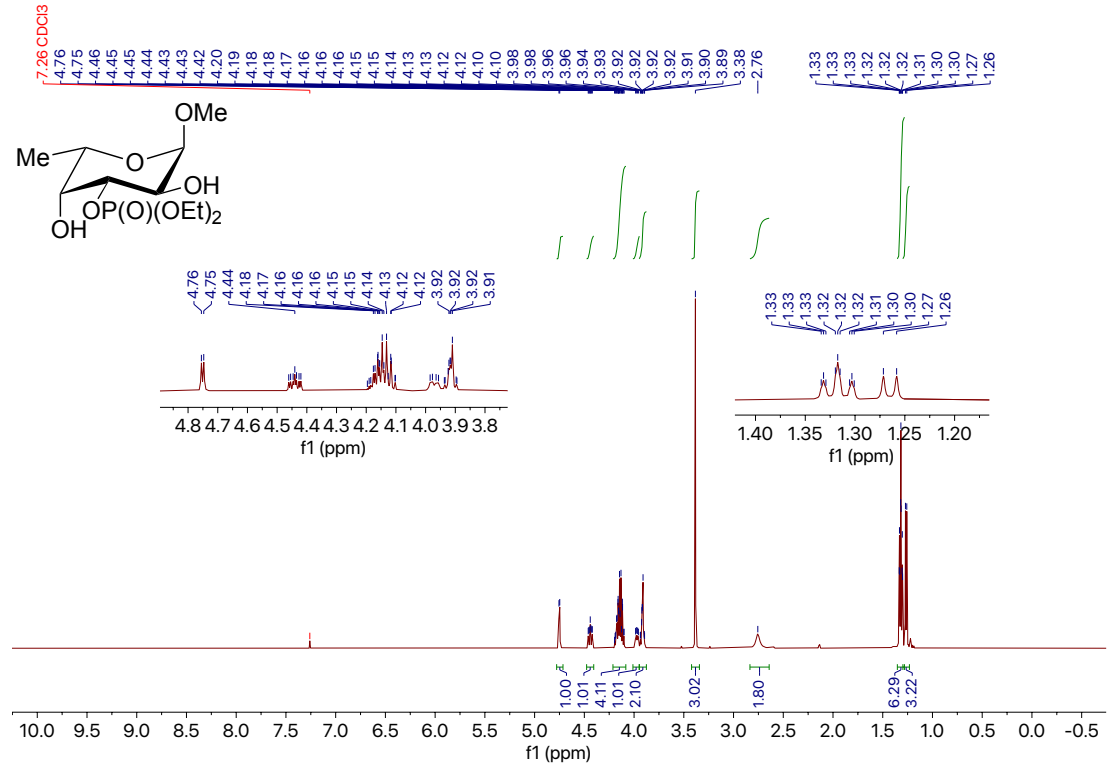
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*R*,3*R*,4*R*,5*S*,6*S*)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl diethyl phosphate (2m)** in $CDCl_3$

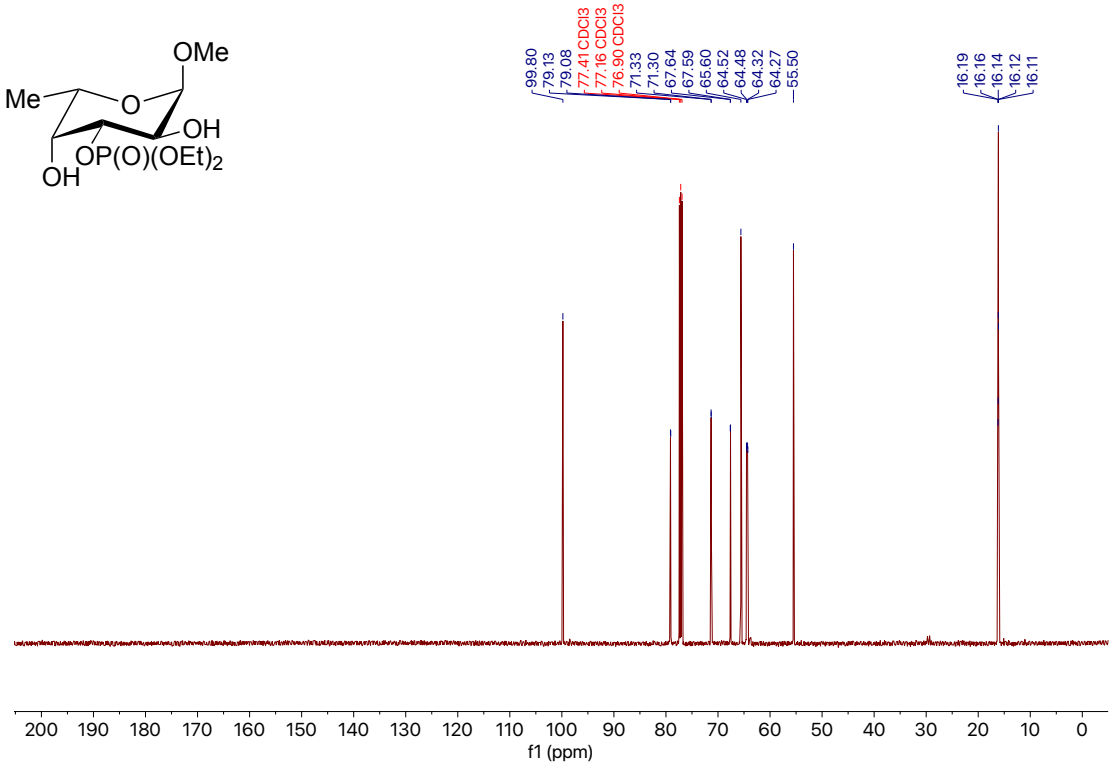


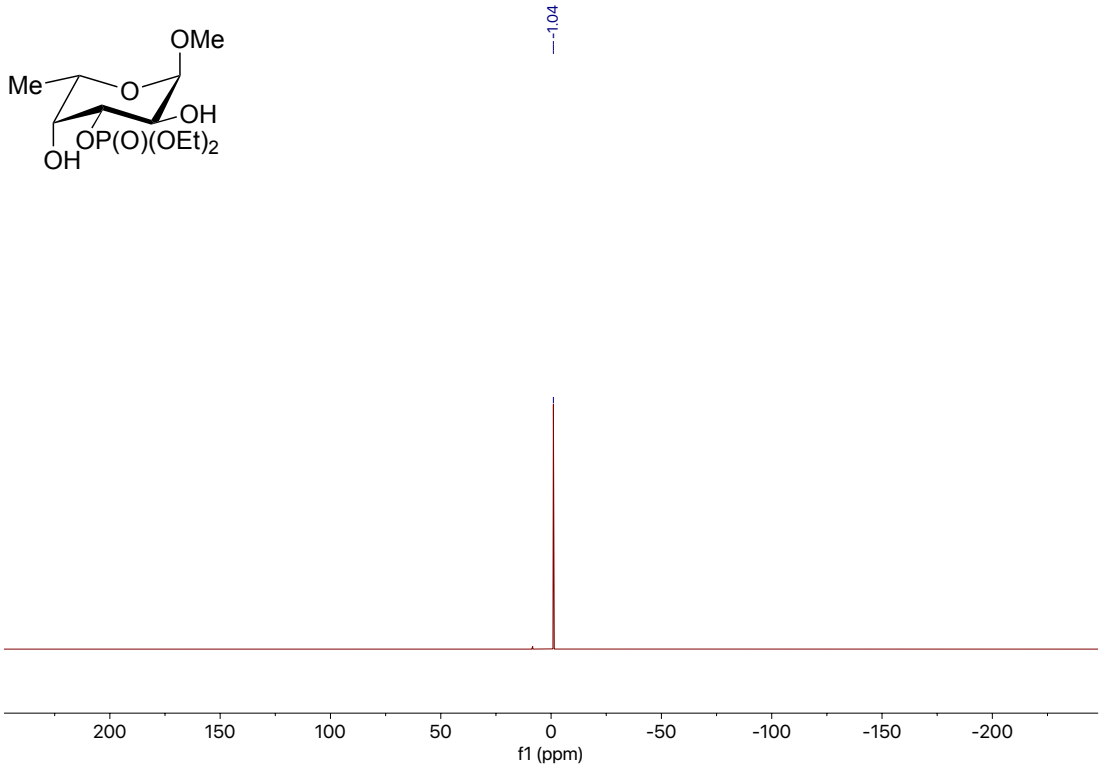

OMe
Me
HO
O
(EtO)2(O)PO
OH
100.55
80.15
80.10
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
71.63
71.60
70.22
70.18
68.13
64.79
64.75
54.95
17.71
16.24
16.22
16.19
16.17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OMe
Me
HO
O
(EtO)2(O)PO
OH
0.12
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

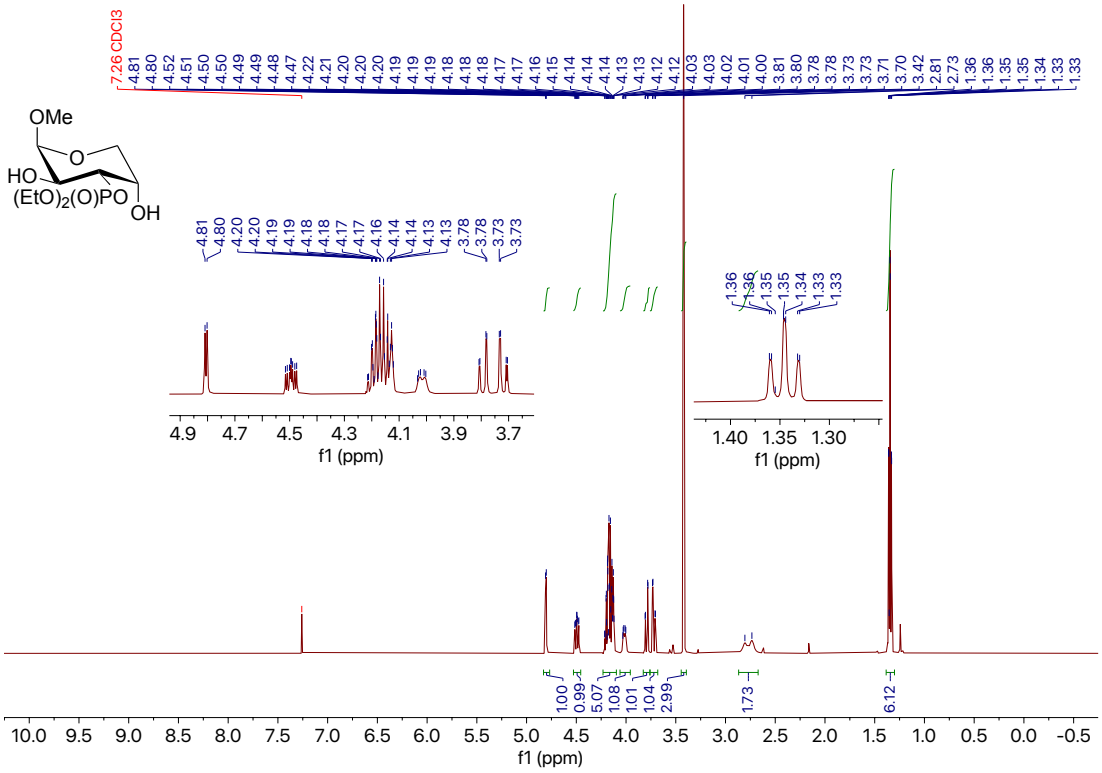
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*R*,3*S*,4*R*,5*R*,6*S*)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl diethyl phosphate (2n)** in $CDCl_3$

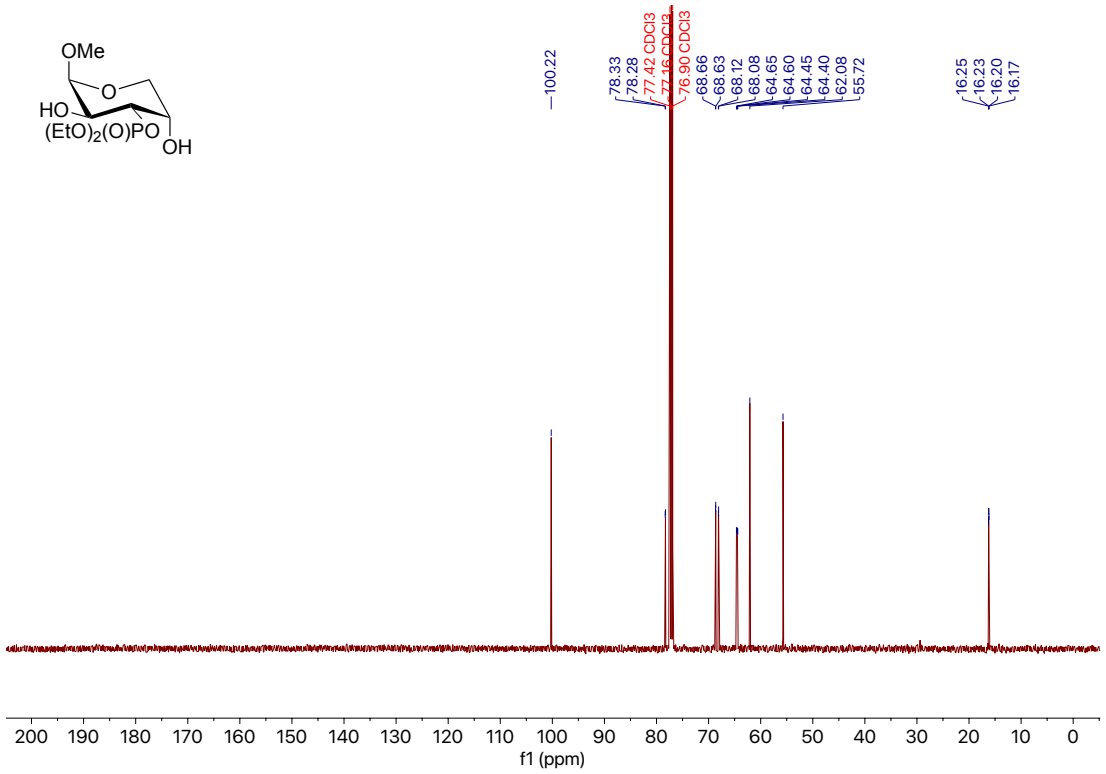


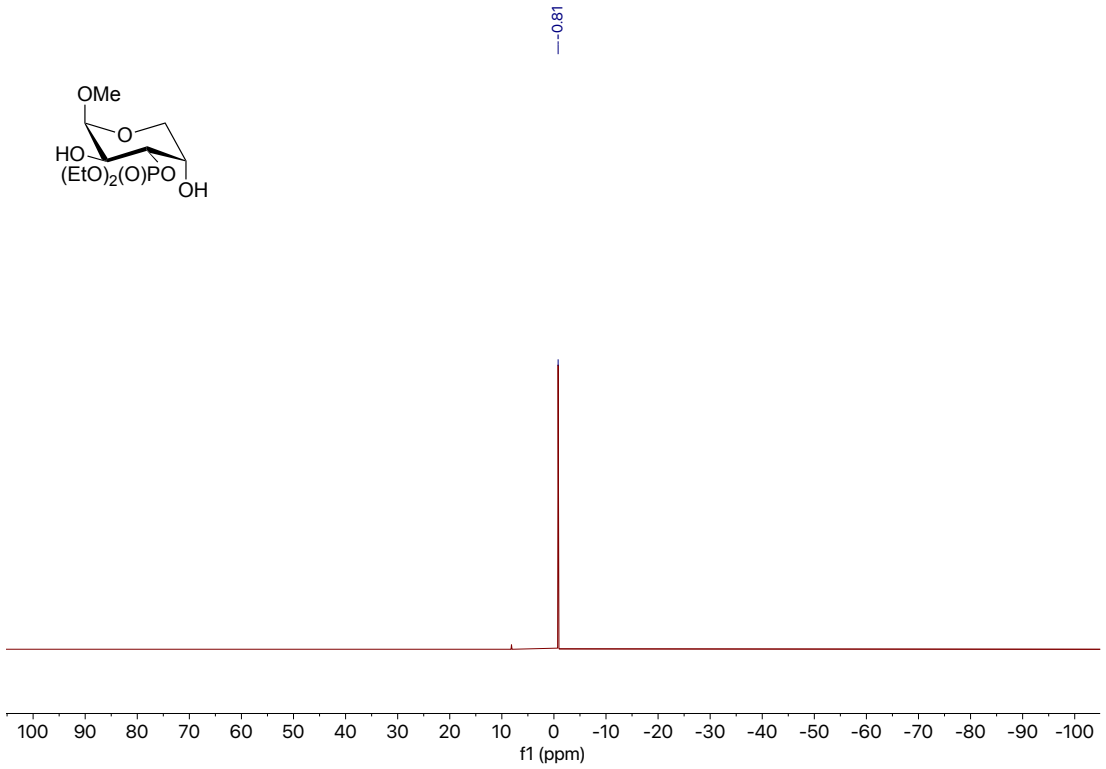




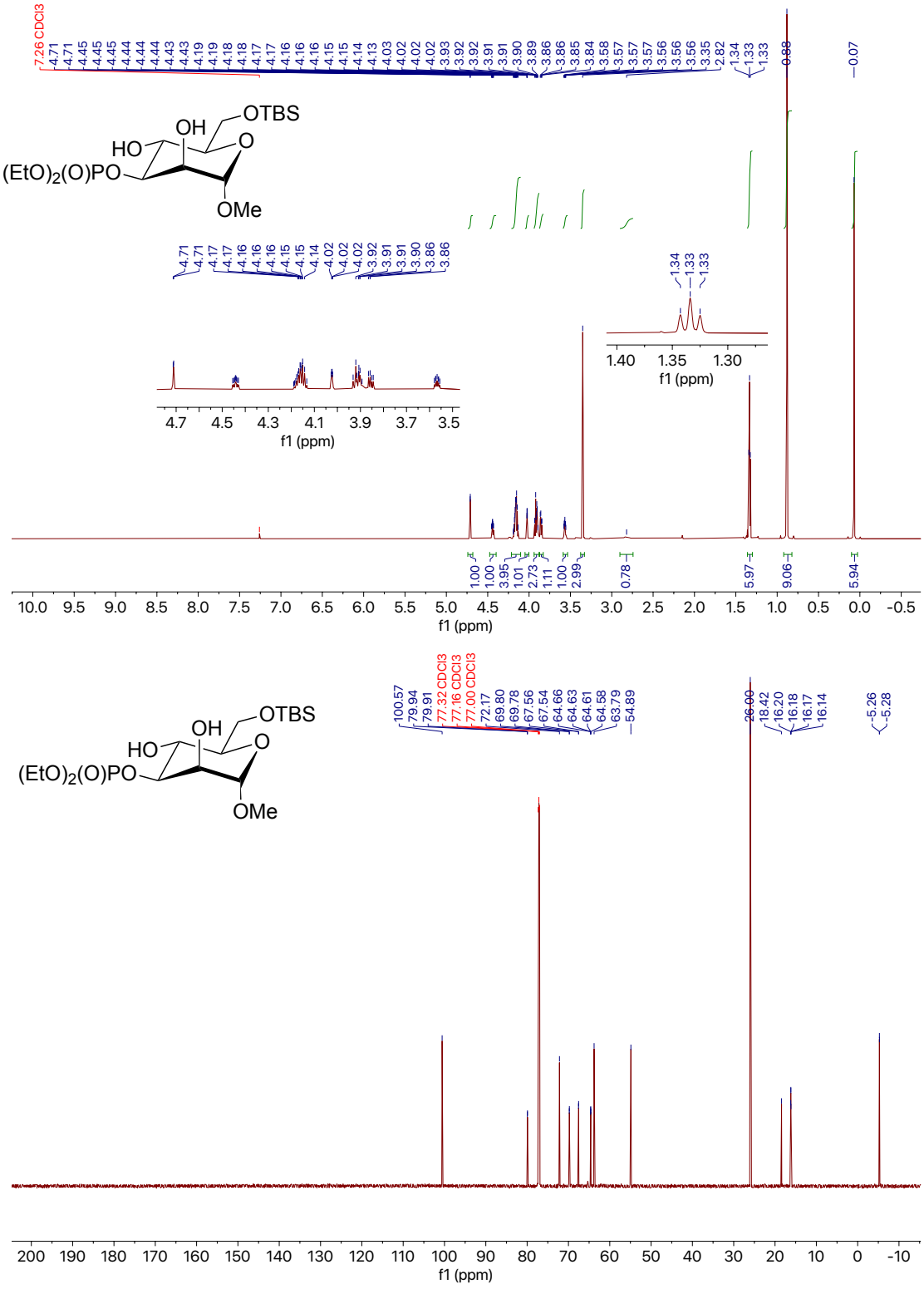
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*S*,3*R*,4*S*,5*S*)-3,5-dihydroxy-2-methoxytetrahydro-2H-pyran-4-yl diethyl phosphate (2o)** in $CDCl_3$

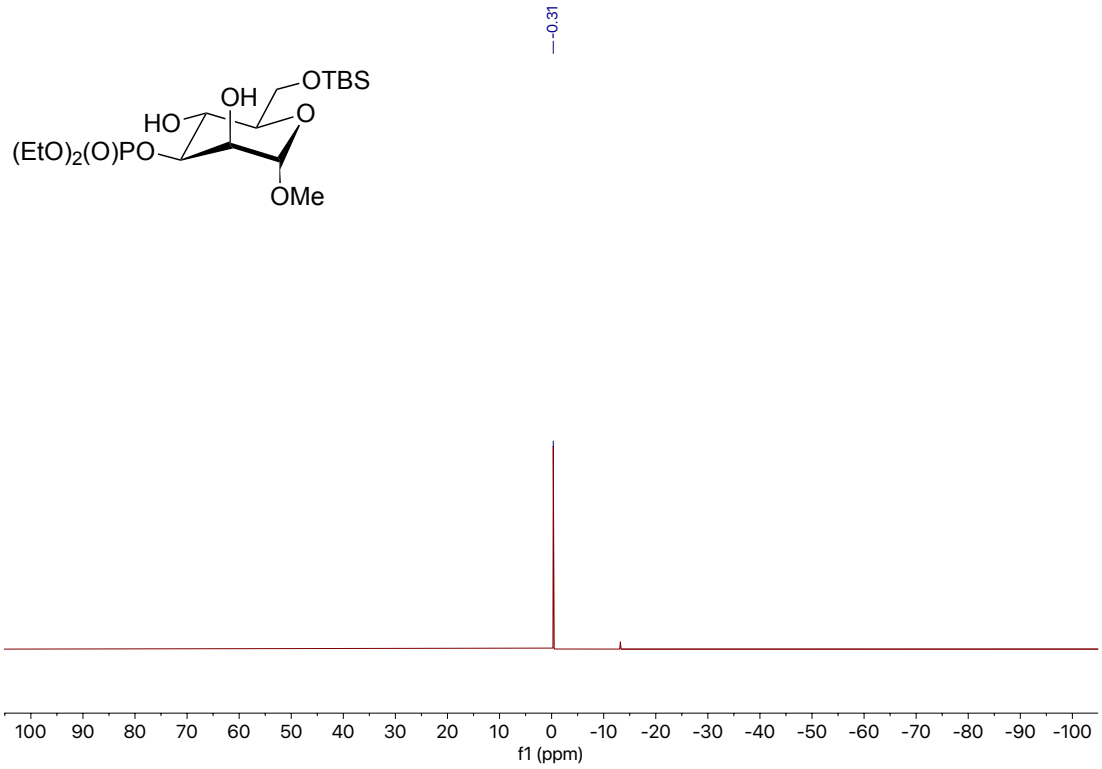



OMe
O
HO
(EtO)2(O)PO
OH
100.22
78.33
78.28
77.42 CDCl3
77.16 CDCl3
76.90 CDCl3
68.66
68.63
68.12
68.08
64.65
64.60
64.45
64.40
62.08
55.72
16.25
16.23
16.20
16.17
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

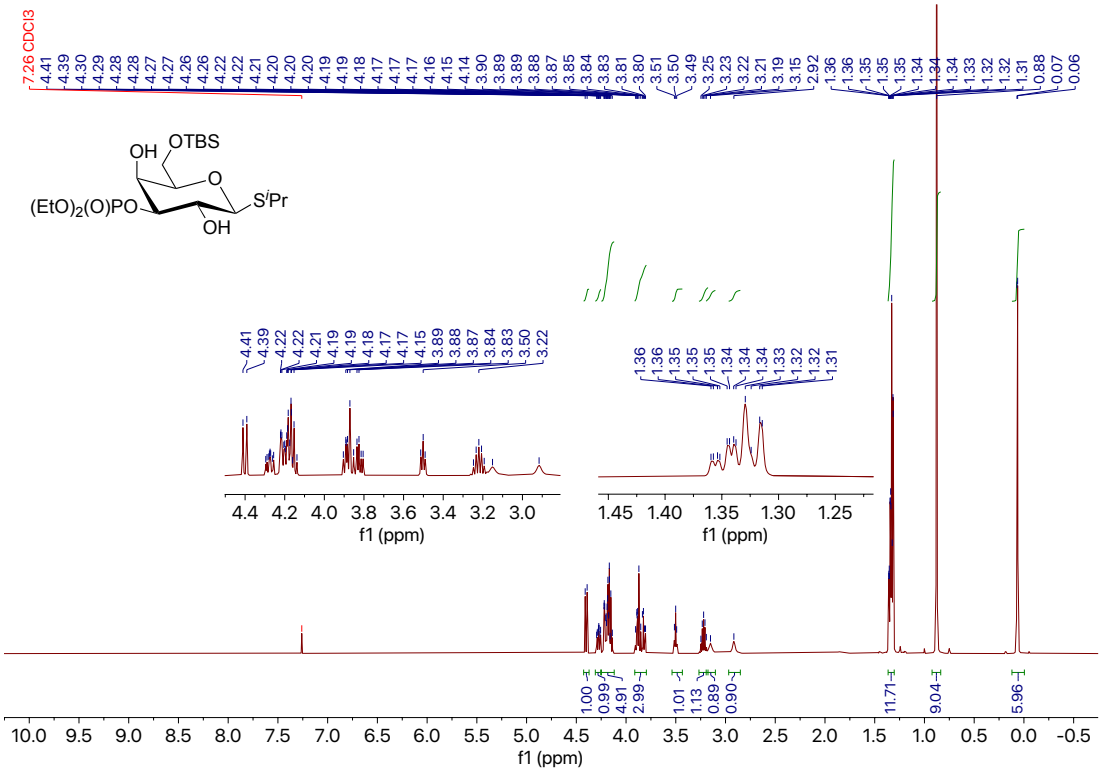

0.81
OMe
O
HO
(EtO)2(O)PO
OH
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

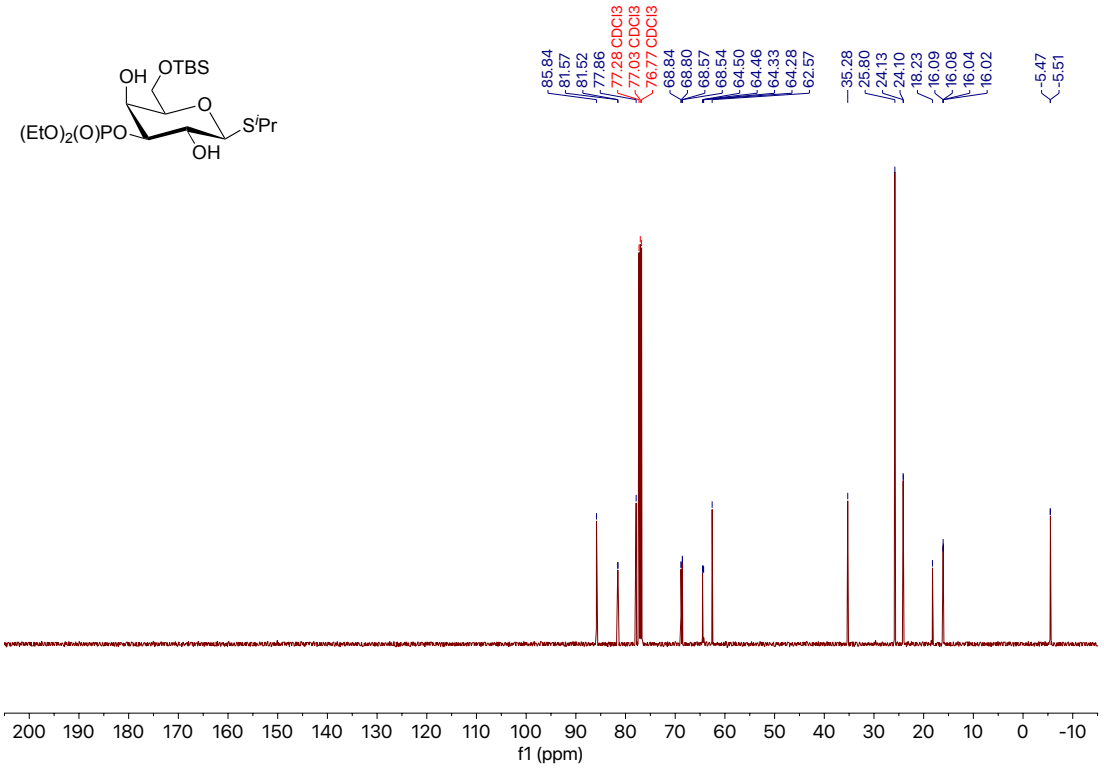
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(((tert-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-methoxytetrahydro-2H-pyran-4-yl diethyl phosphate (2p)** in $CDCl_3$

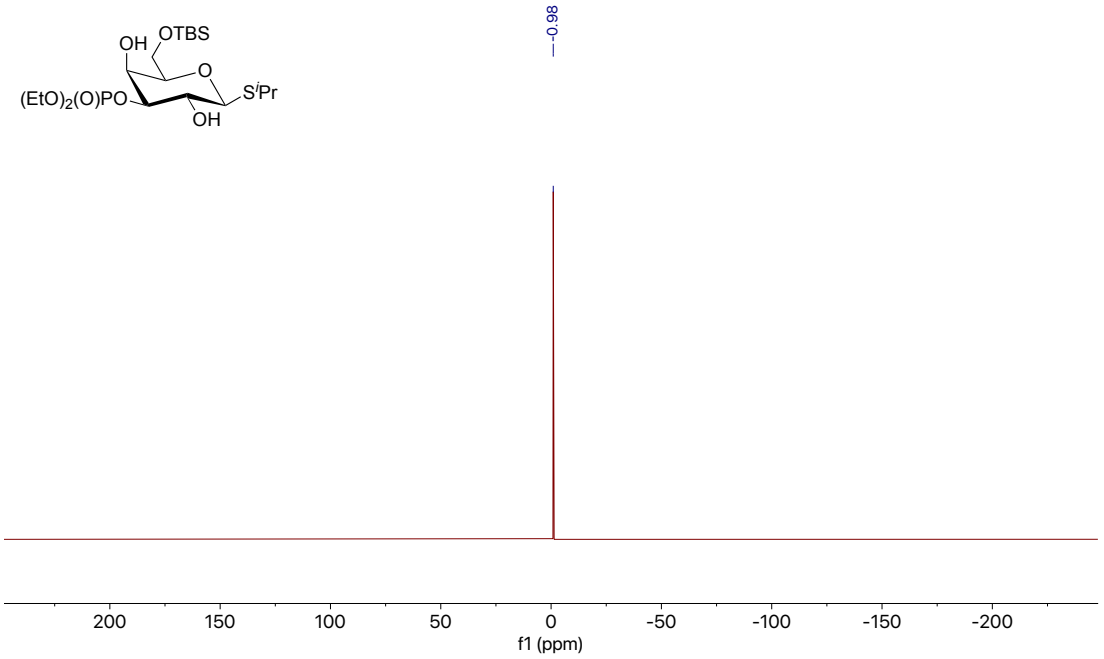




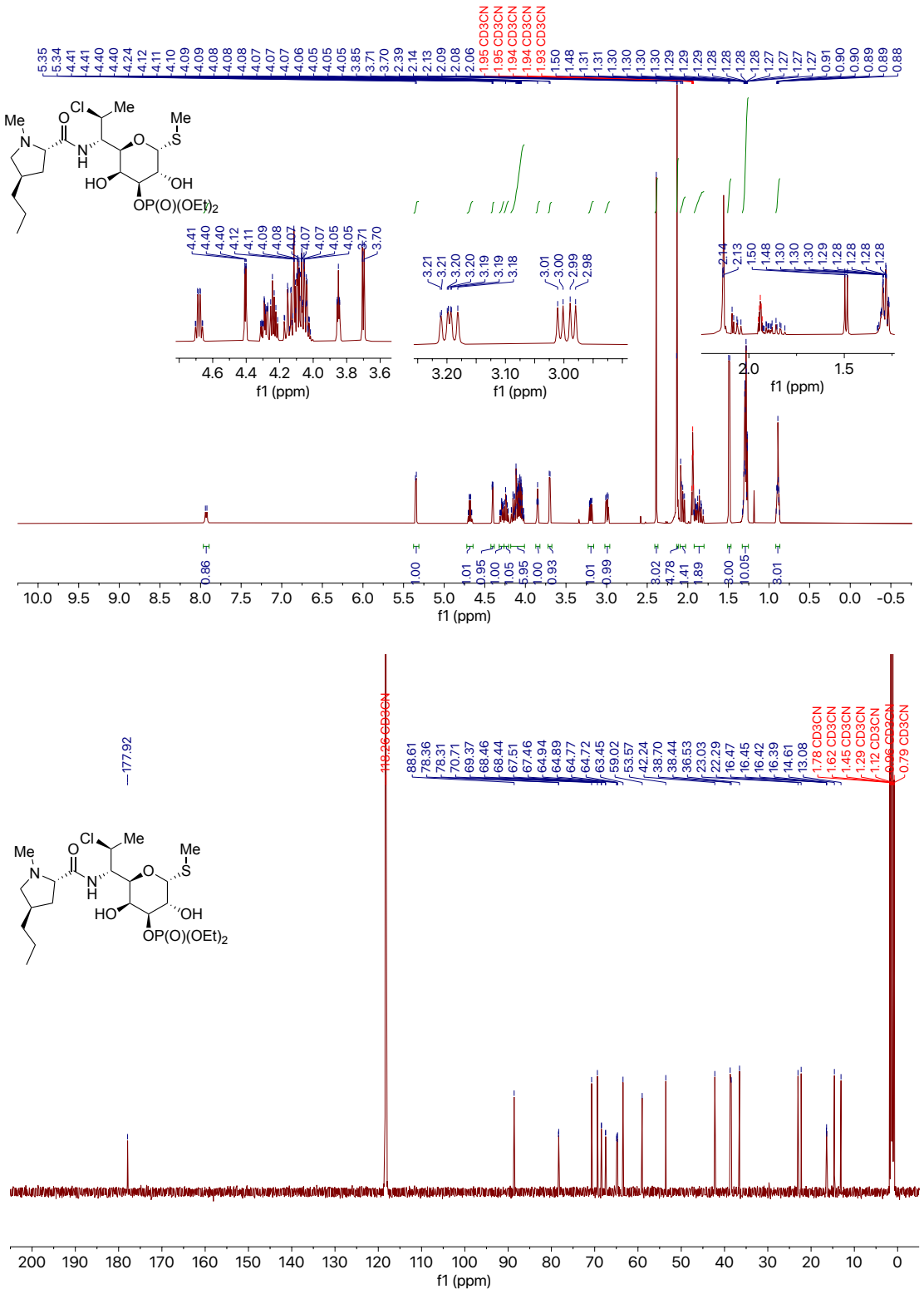
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2R,3S,4S,5R,6S)-2-(((tert-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-(isopropylthio)tetrahydro-2H-pyran-4-yl diethyl phosphate (2q)** in $CDCl_3$

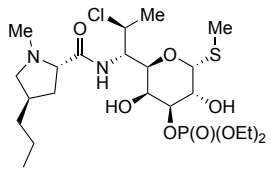



OH
OTBS
O
S^{i}Pr
(EtO)$_2$(O)PO
OH
85.84
81.57
81.52
77.86
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
68.84
68.80
68.57
68.54
64.50
64.46
64.33
64.28
62.57
35.28
25.80
24.13
24.10
18.23
16.09
16.08
16.04
16.02
-5.47
-5.51
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

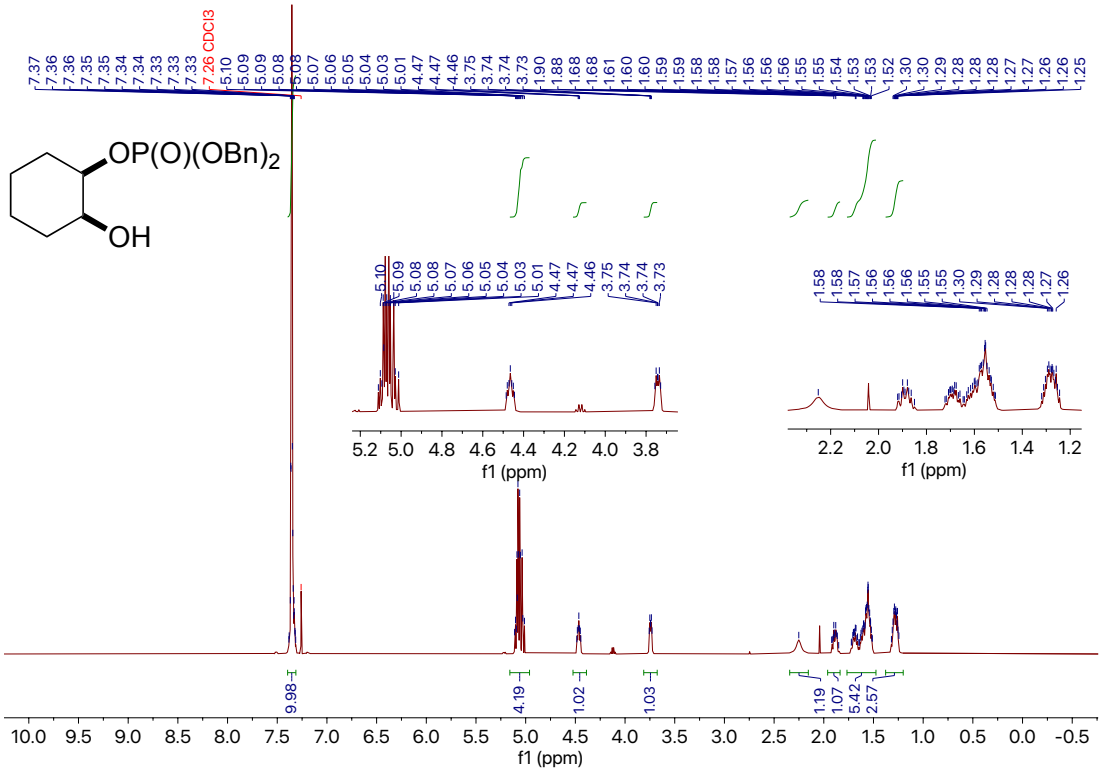

OH
OTBS
O
S^{i}Pr
(EtO)$_2$(O)PO
OH
-0.98
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

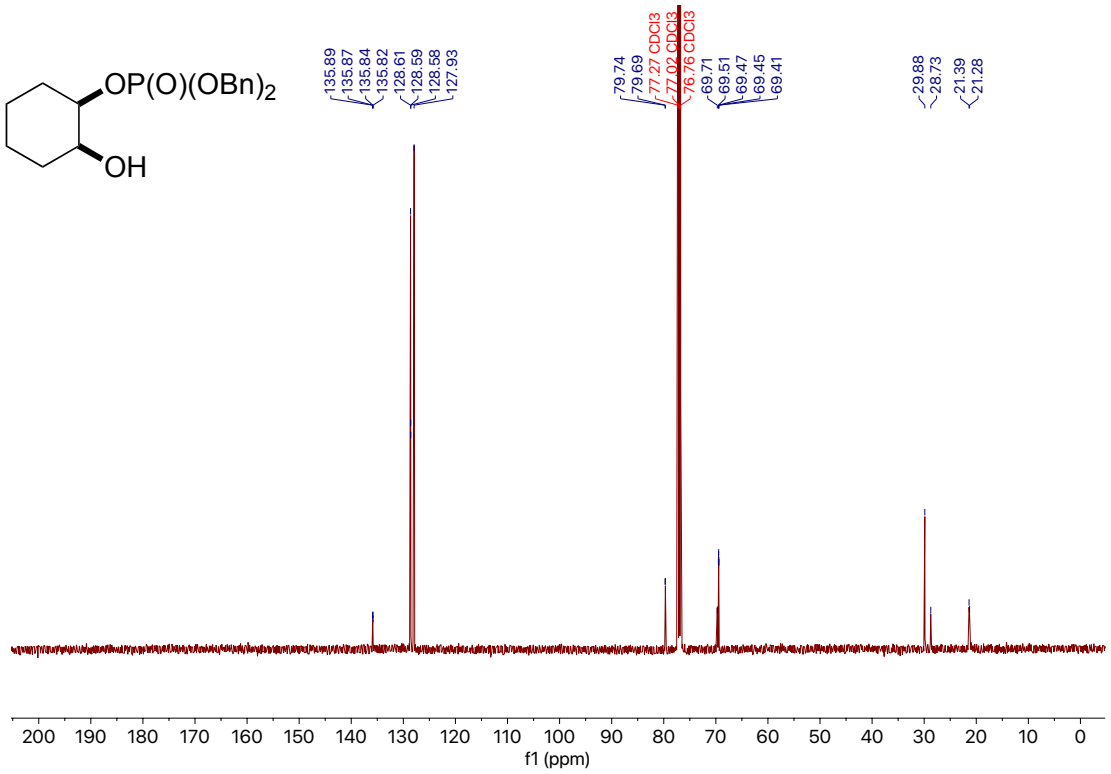
^{1}H, ^{13}C{^{1}H}, and ^{31}P{1H} NMR for **(2*S*,3*S*,4*S*,5*R*,6*R*)-2-((1*S*)-2-chloro-1-((4*R*)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl diethyl phosphate (2r)** in $CDCl_3$

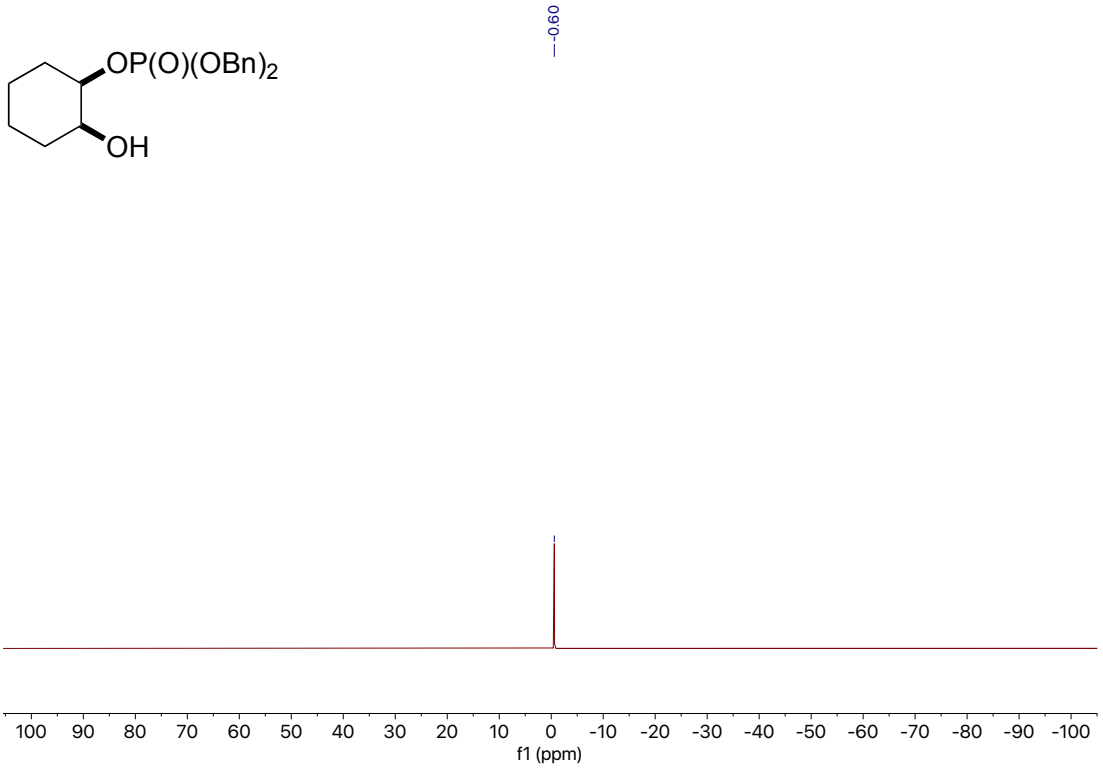




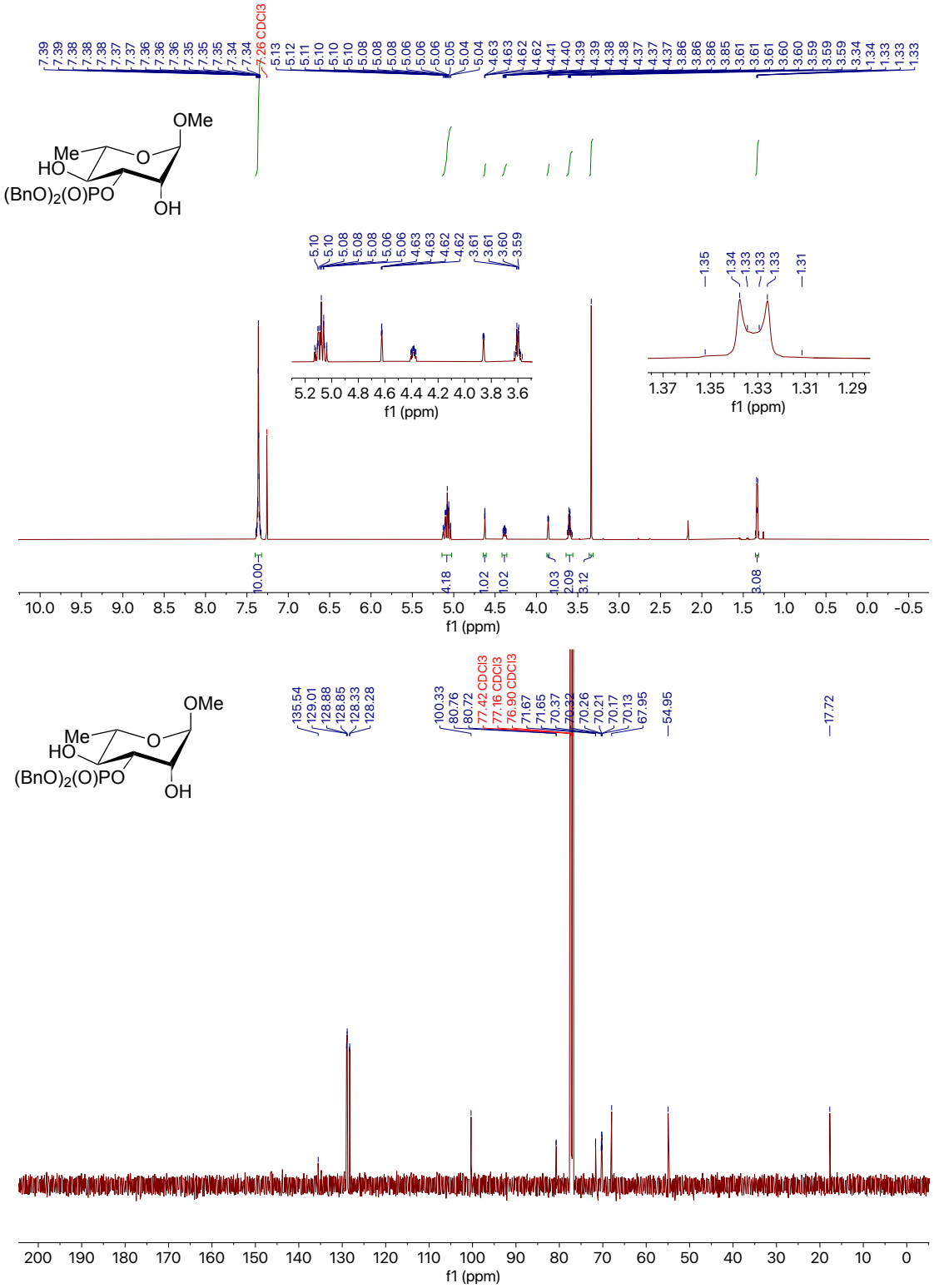
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Dibenzyl (2-hydroxycyclohexyl) phosphate (4a)** in $CDCl_3$

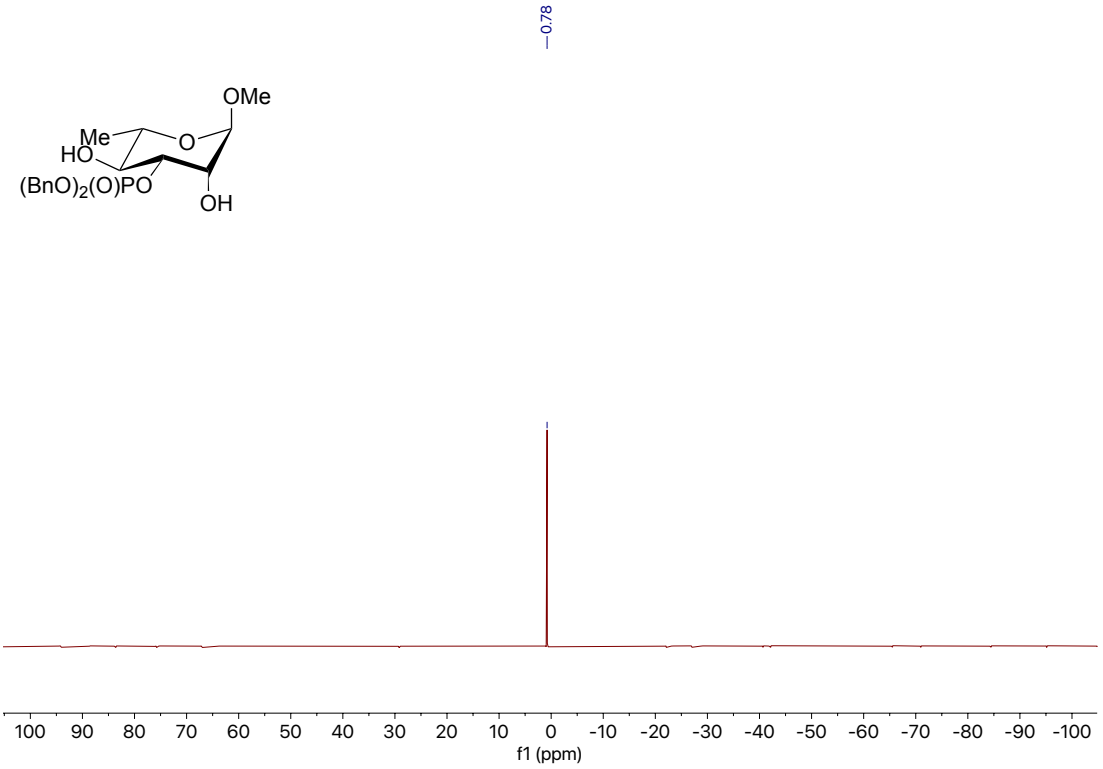



OP(O)(OBn)2
OH
135.89
135.87
135.84
135.82
128.61
128.59
128.58
127.93
79.74
79.69
77.27 CDCl3
77.02 CDCl3
76.76 CDCl3
69.71
69.51
69.47
69.45
69.41
29.88
28.73
21.39
21.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

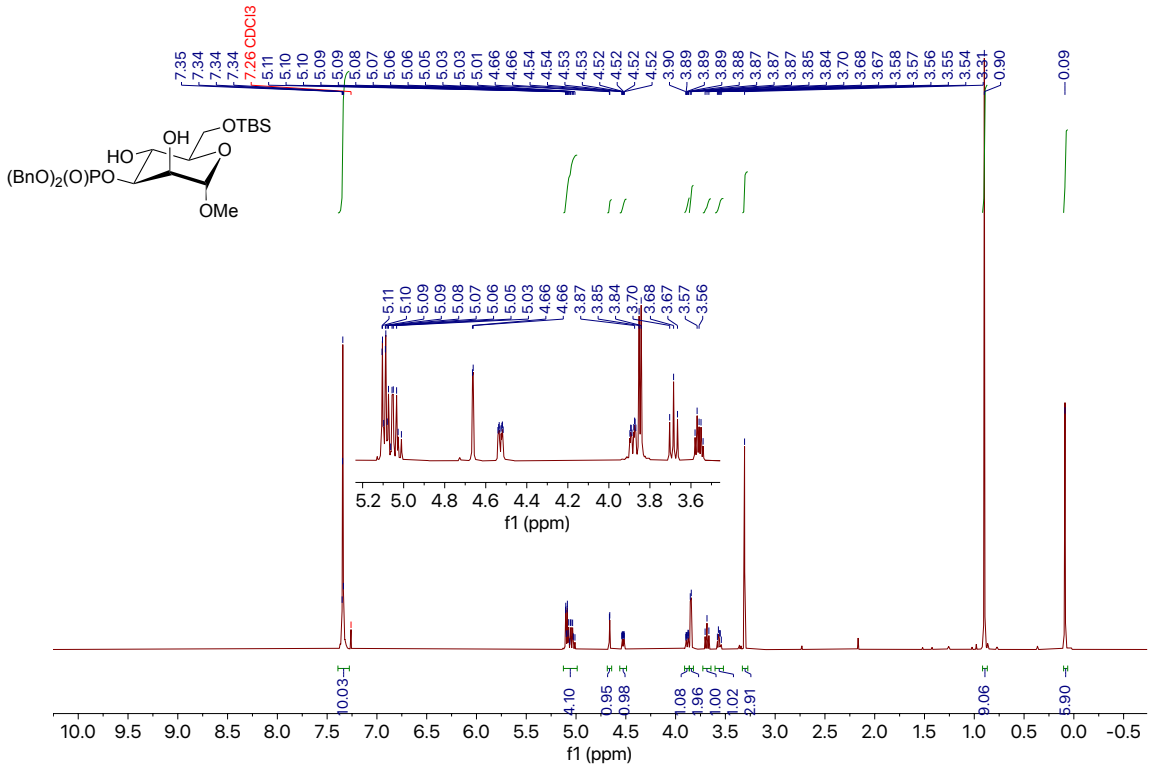

OP(O)(OBn)2
OH
-0.60
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

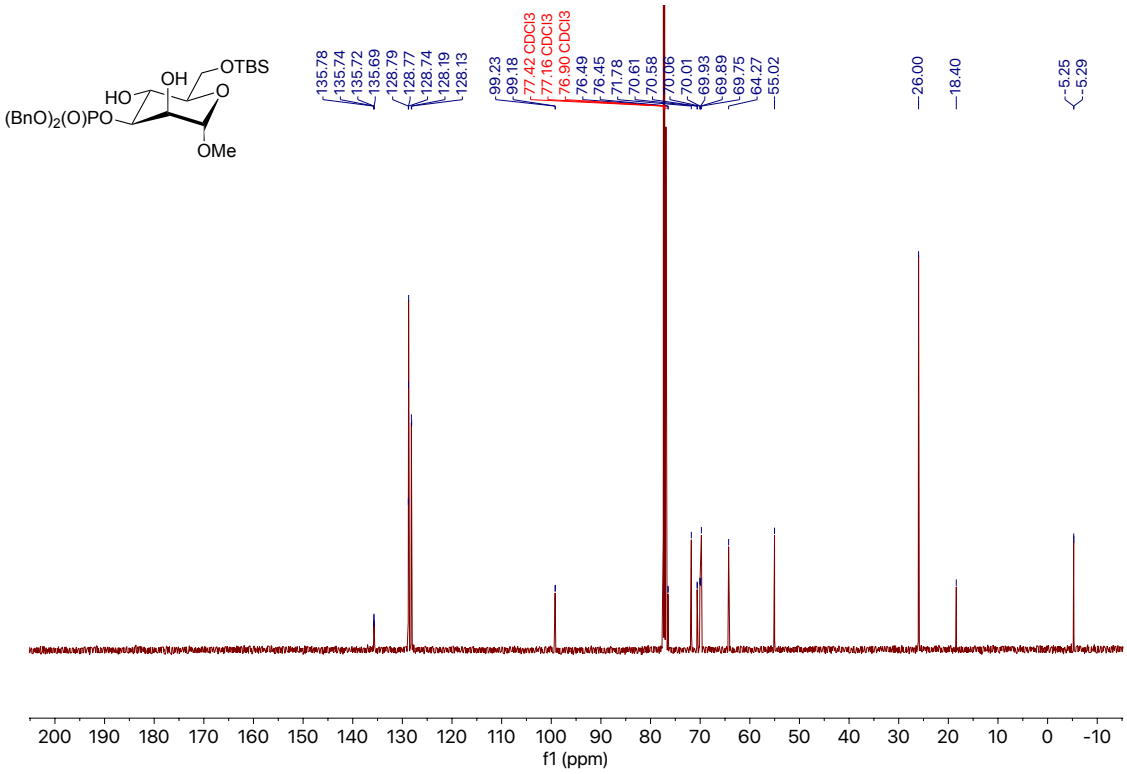
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Dibenzyl ((2R,3R,4R,5S,6S)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl) phosphate (4m)** in $CDCl_3$

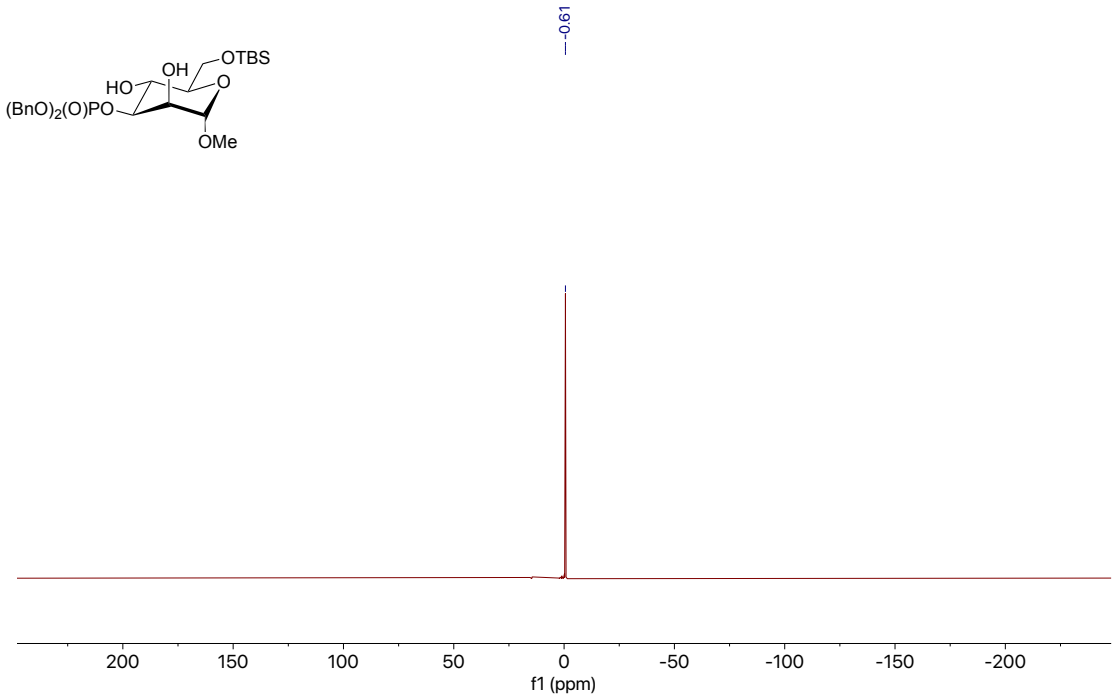




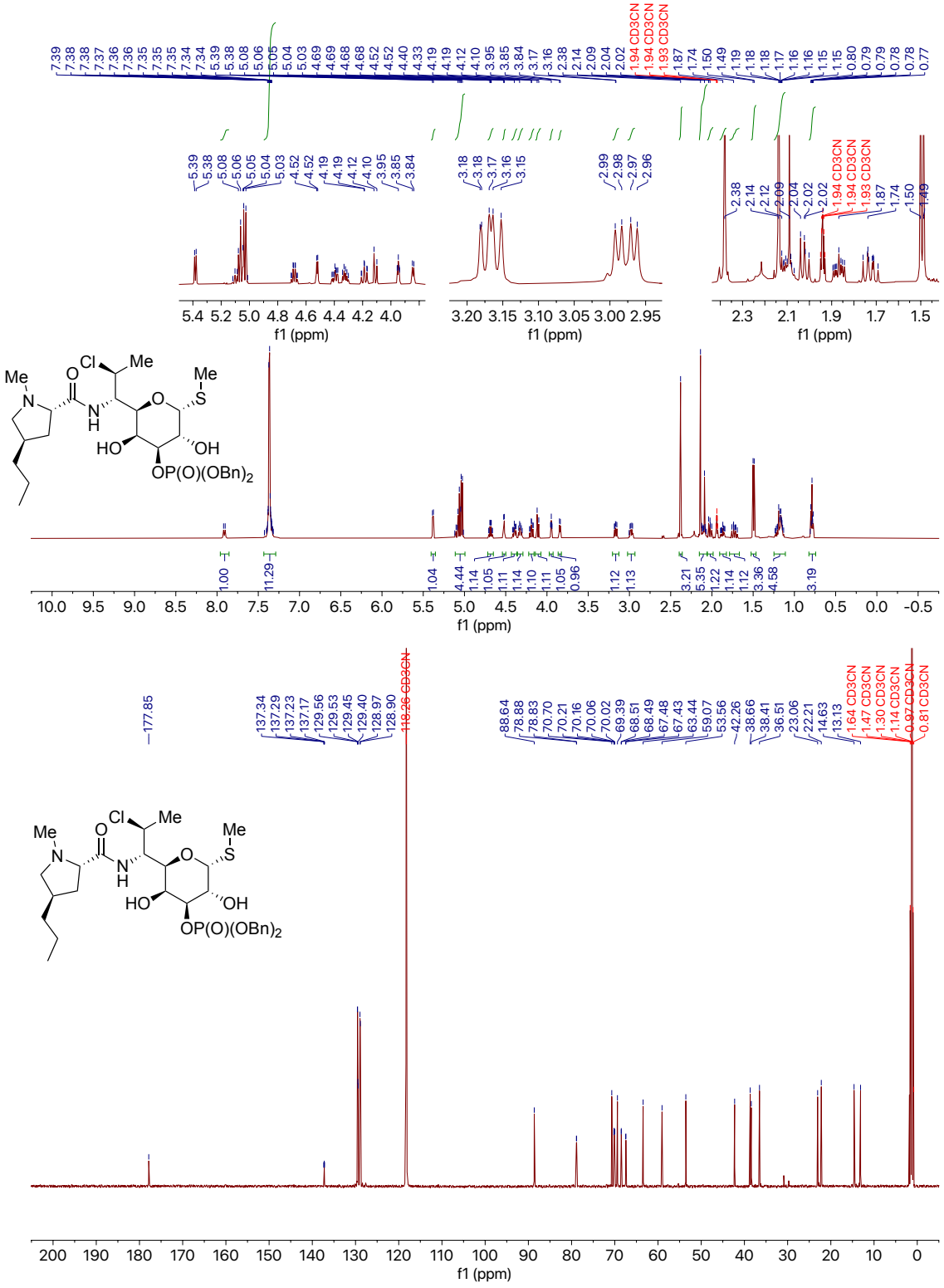
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Dibenzyl ((2*R*,3*R*,4*S*,5*S*,6*S*)-2-(((tert-butyldimethylsilyl)oxy)methyl)-3,5-dihydroxy-6-methoxytetrahydro-2H-pyran-4-yl) phosphate (4p)** in $CDCl_3$

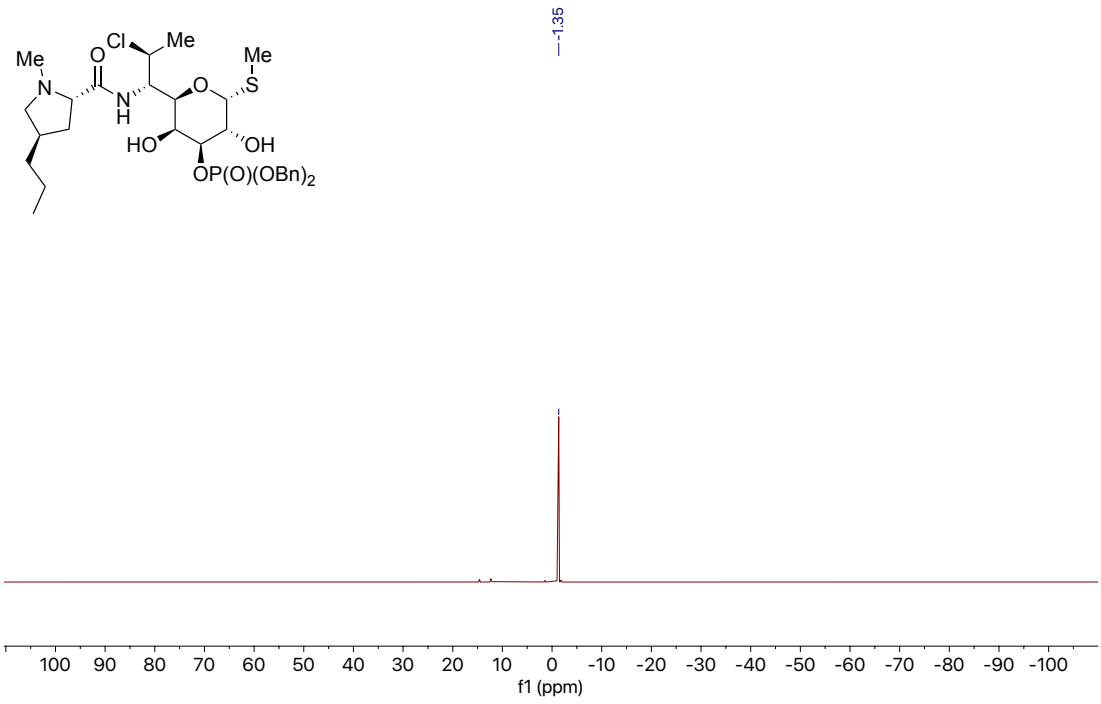



OTBS
OH
HO
O
(BnO)2(O)PO
OMe
135.78
135.74
135.72
135.69
128.79
128.77
128.74
128.19
128.13
99.23
99.18
77.42 CDCl3
77.16 CDCl3
76.90 CDCl3
76.49
76.45
71.78
70.61
70.58
70.06
70.01
69.93
69.89
69.75
64.27
55.02
26.00
18.40
-5.25
-5.29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

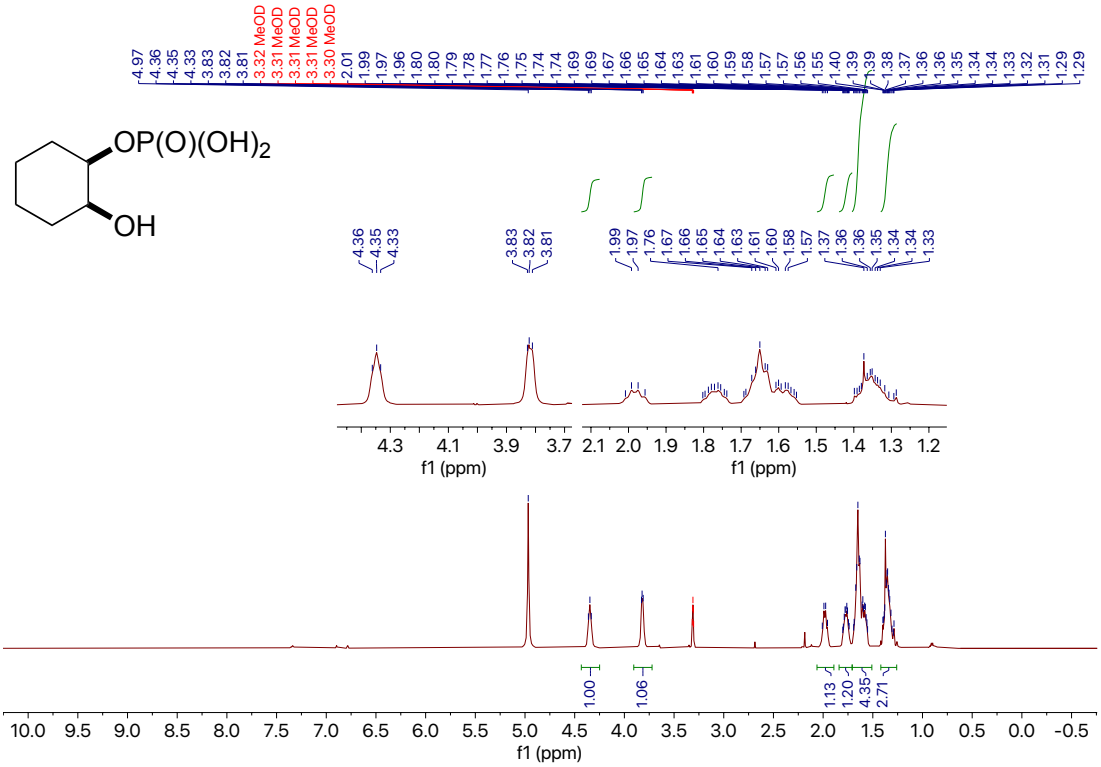

OTBS
OH
HO
O
(BnO)2(O)PO
OMe
-0.61
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

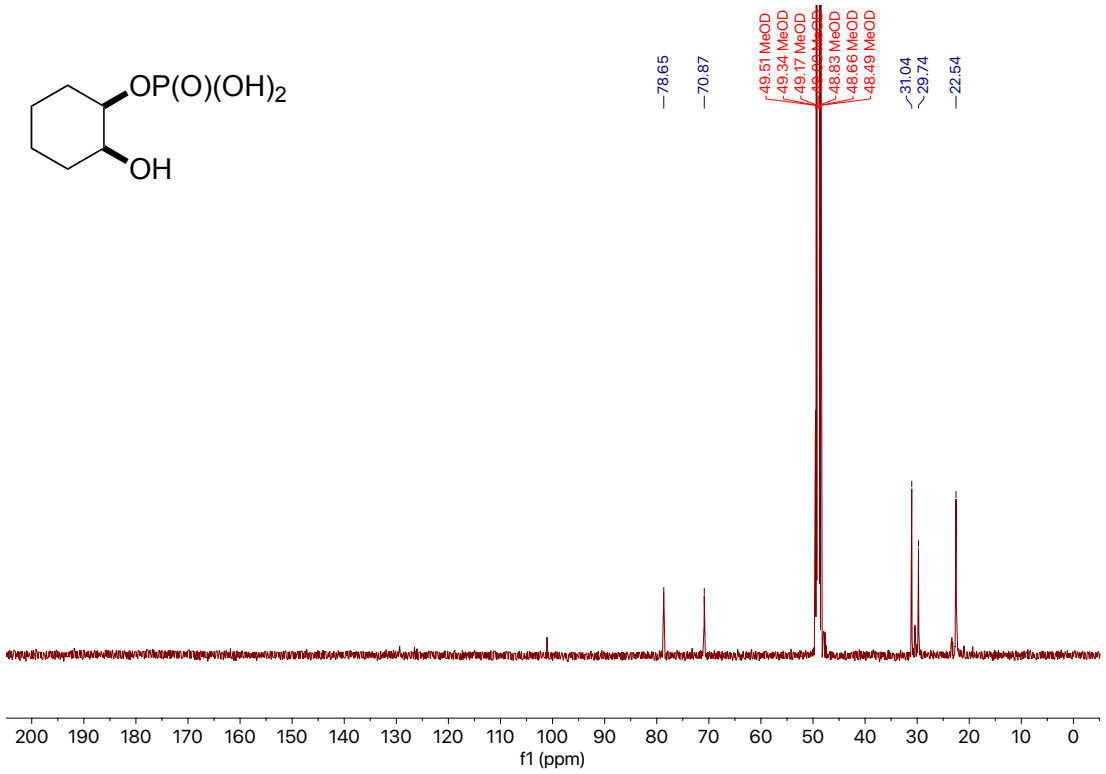
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **Dibenzyl ((2R,3S,4S,5R,6R)-2-((1R,2S)-2-chloro-1-((2R,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl) phosphate (4r)** in CD_3CN

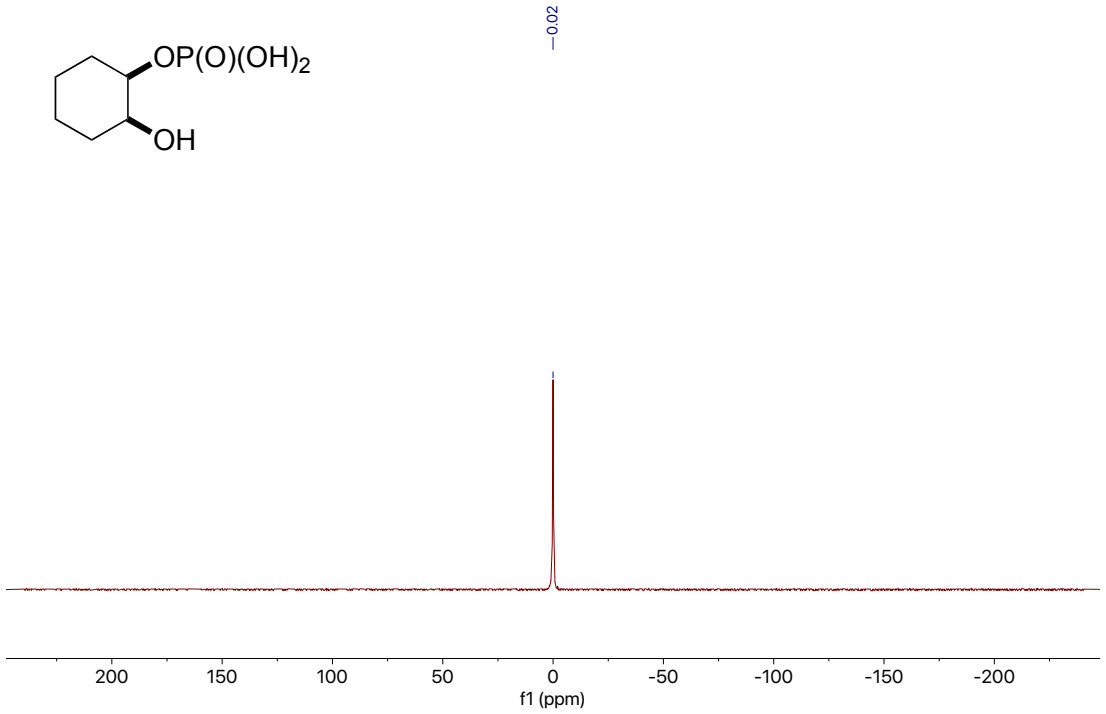




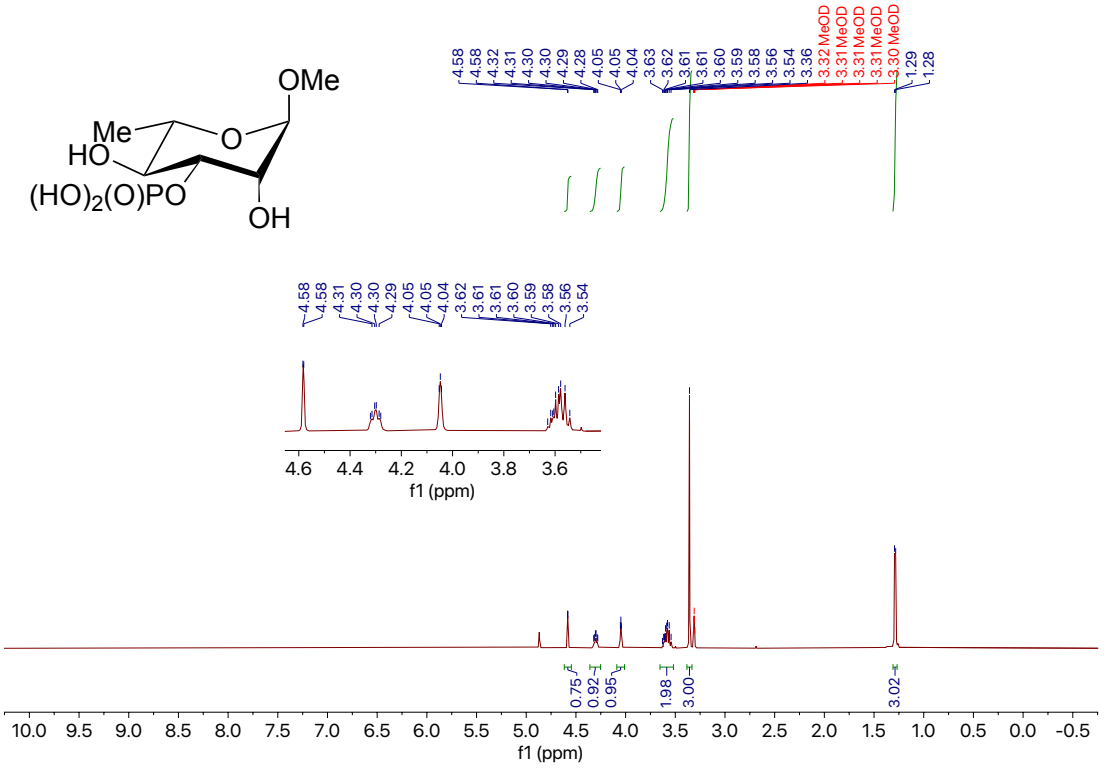
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **2-Hydroxycyclohexyl dihydrogen phosphate (5a)** in CD_3OD

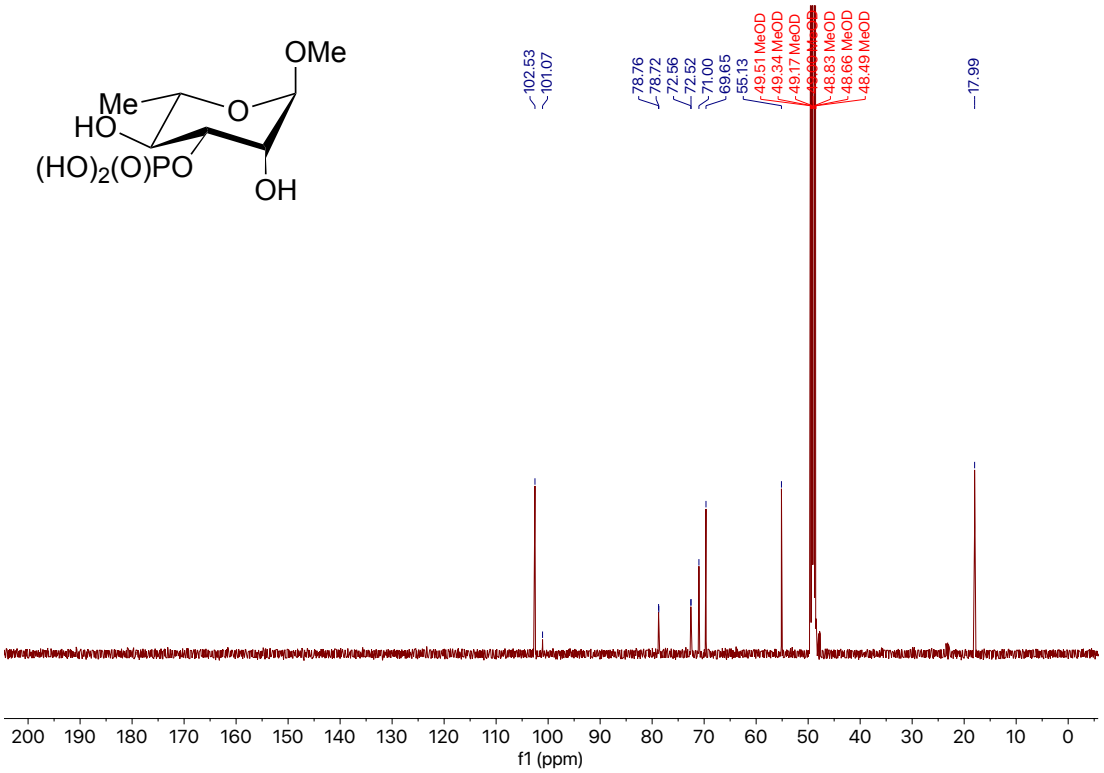


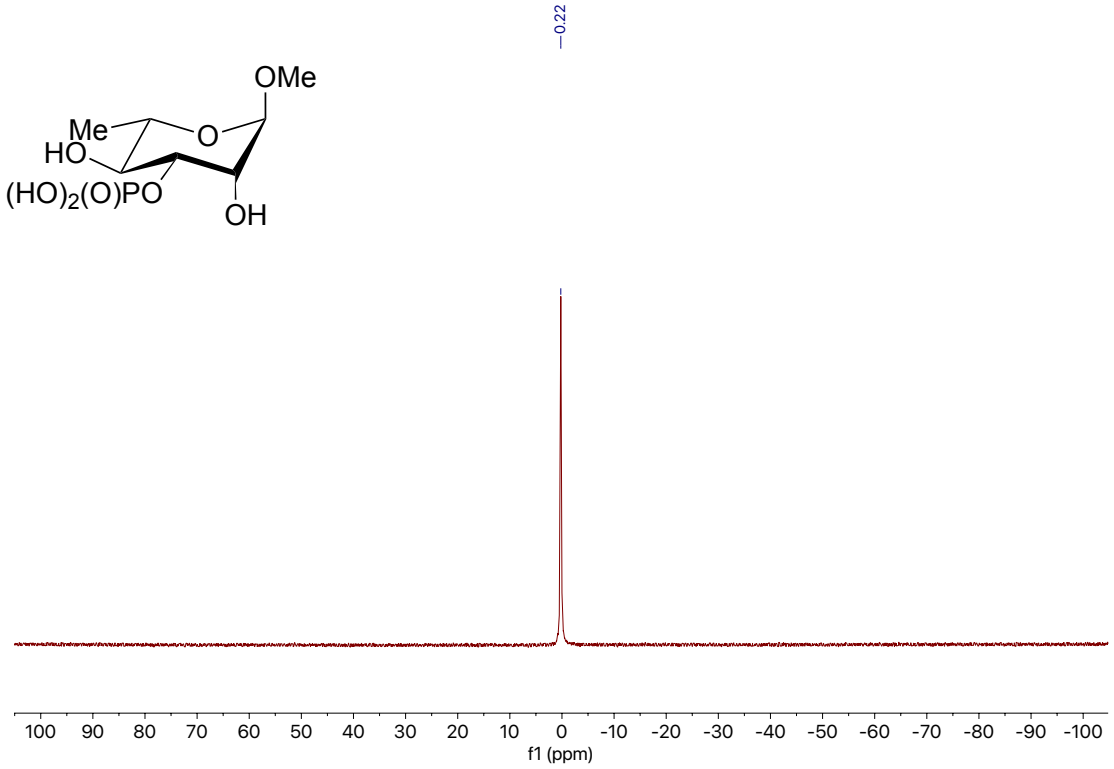

OP(O)(OH)2
OH
78.65
70.87
49.51 MeOD
49.34 MeOD
49.17 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
31.04
29.74
22.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OP(O)(OH)2
OH
0.02
200 150 100 50 0 -50 -100 -150 -200
f1 (ppm)

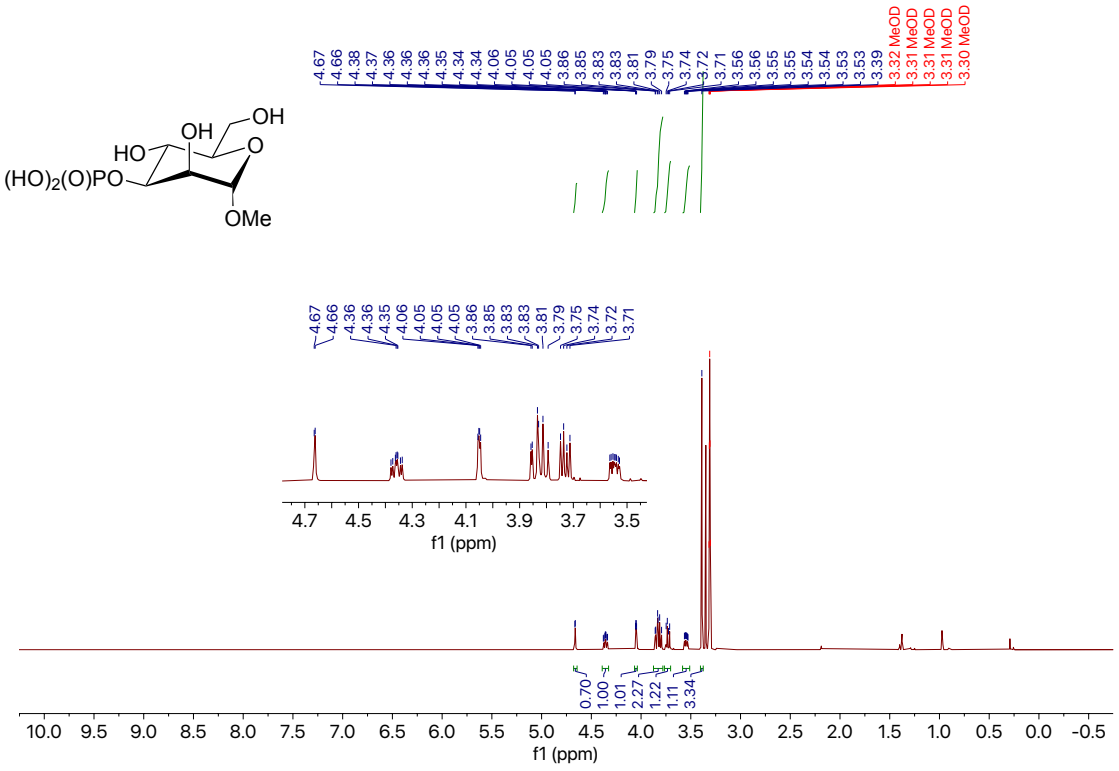
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2R,3R,4R,5S,6S)-3,5-dihydroxy-2-methoxy-6-methyltetrahydro-2H-pyran-4-yl dihydrogen phosphate (5m)** in CD_3OD

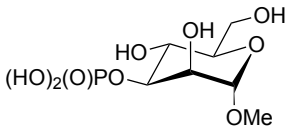




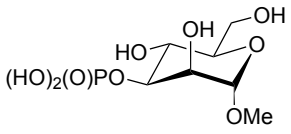


^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-dihydroxy-2-(hydroxymethyl)-6-methoxytetrahydro-2H-pyran-4-yl dihydrogen phosphate (5p)** in CD_3OD



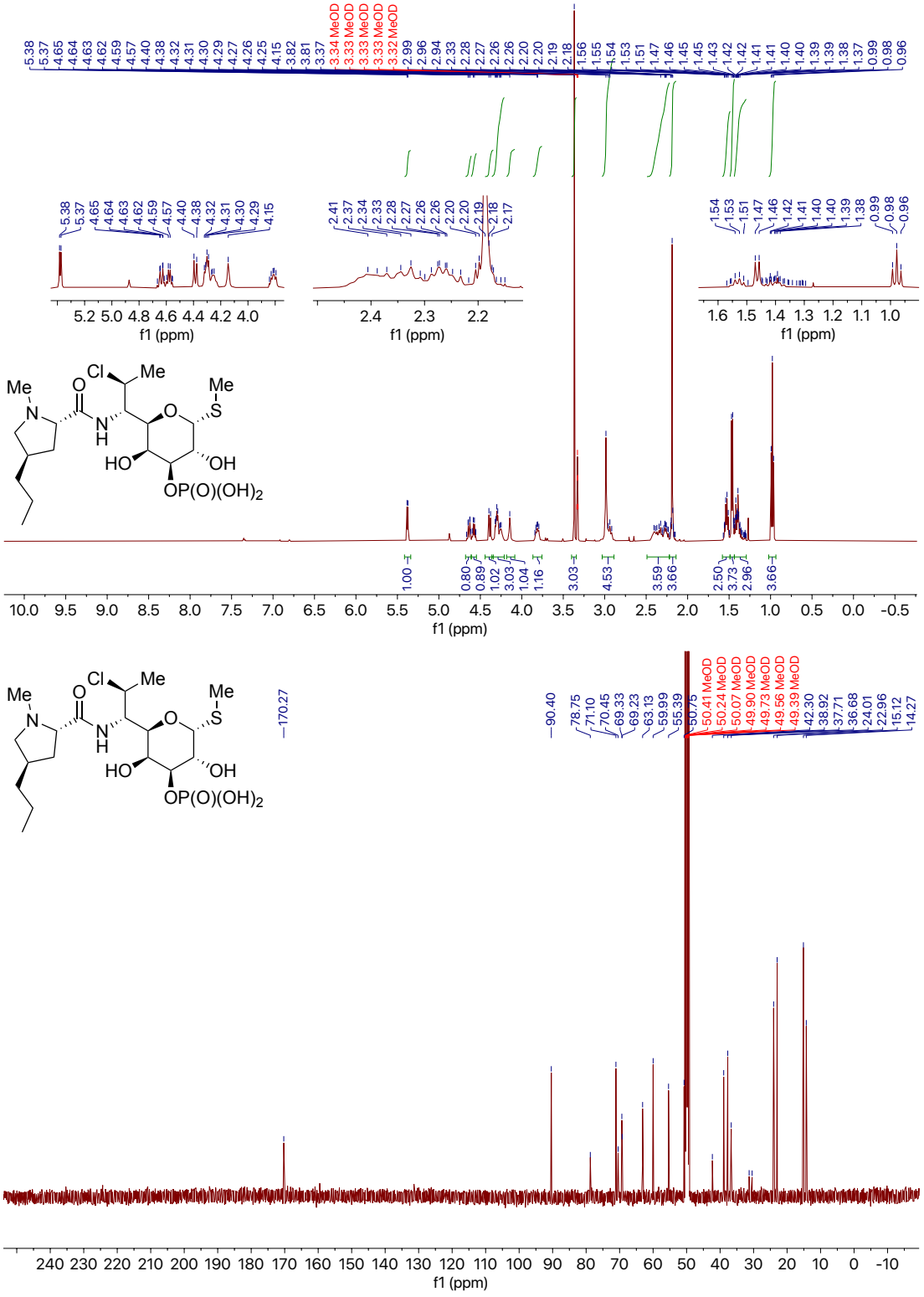

OH
OH
HO
O
(HO)2(O)PO
OMe

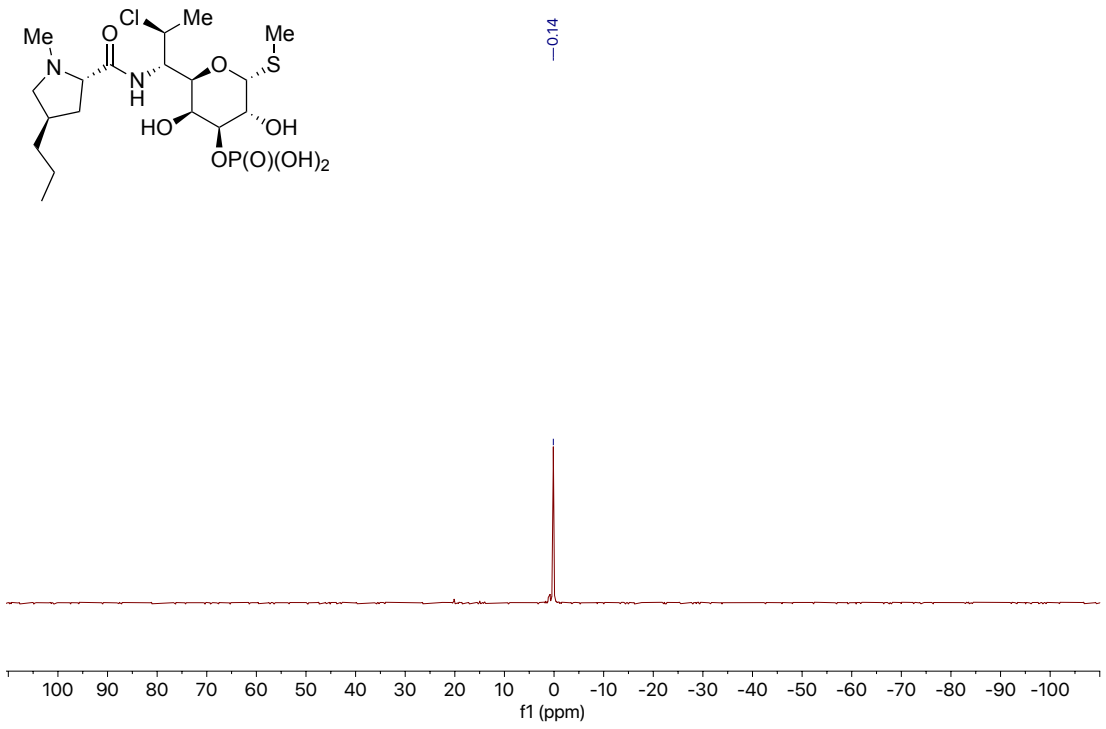
102.47
79.10
79.06
74.44
70.79
67.13
62.68
55.24
49.85
49.51 MeOD
49.34 MeOD
49.17 MeOD
49.00 MeOD
48.83 MeOD
48.66 MeOD
48.49 MeOD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
OH
HO
O
(HO)2(O)PO
OMe

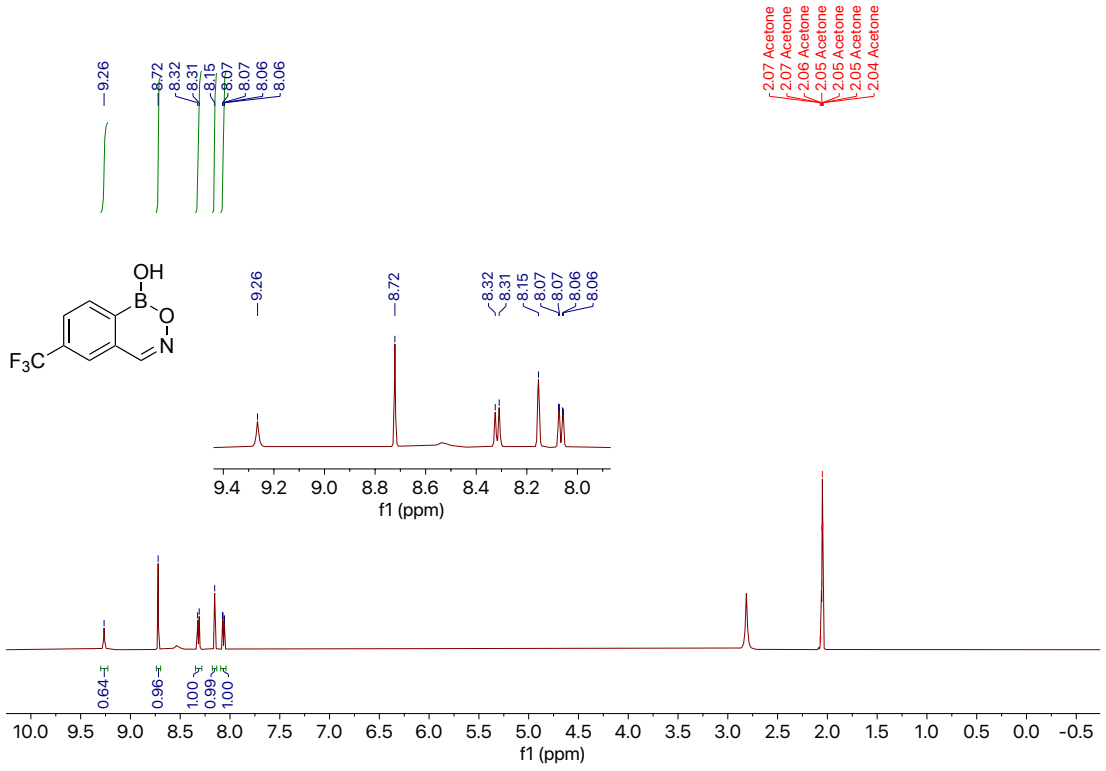
0.14
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

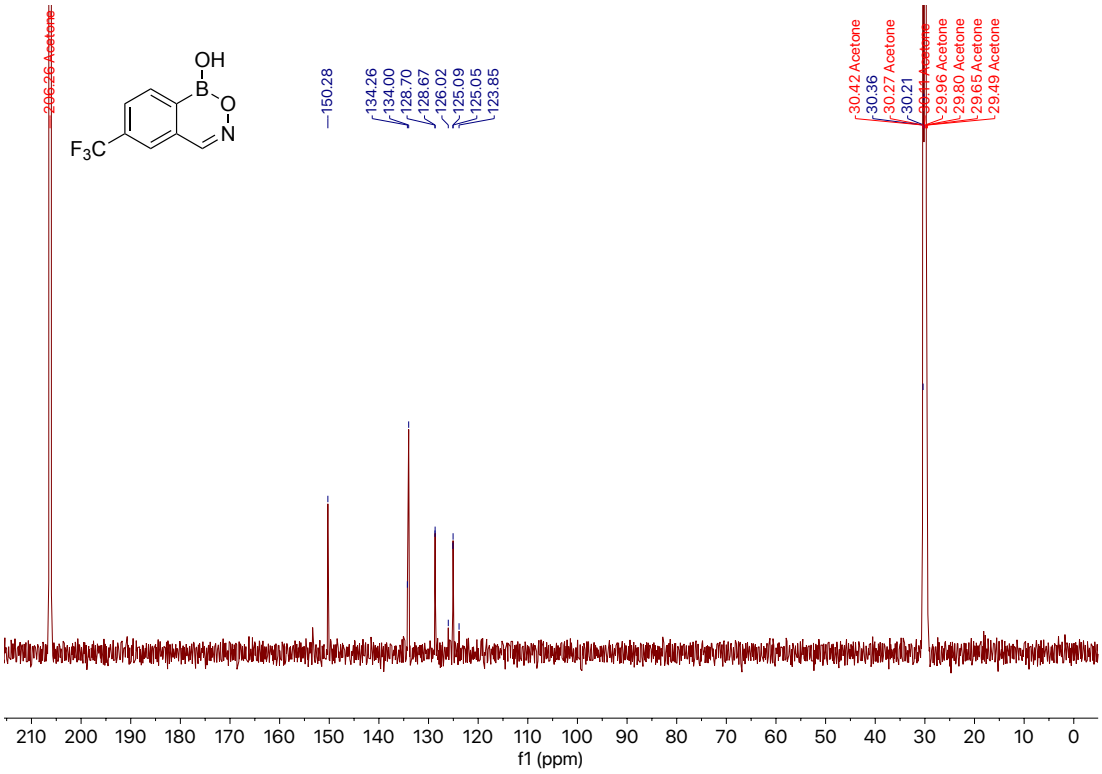
^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR for **(2R,3S,4S,5R,6R)-2-((1R,2S)-2-chloro-1-((2R,4R)-1-methyl-4-propylpyrrolidine-2-carboxamido)propyl)-3,5-dihydroxy-6-(methylthio)tetrahydro-2H-pyran-4-yl dihydrogen phosphate (5r)** in CD_3OD

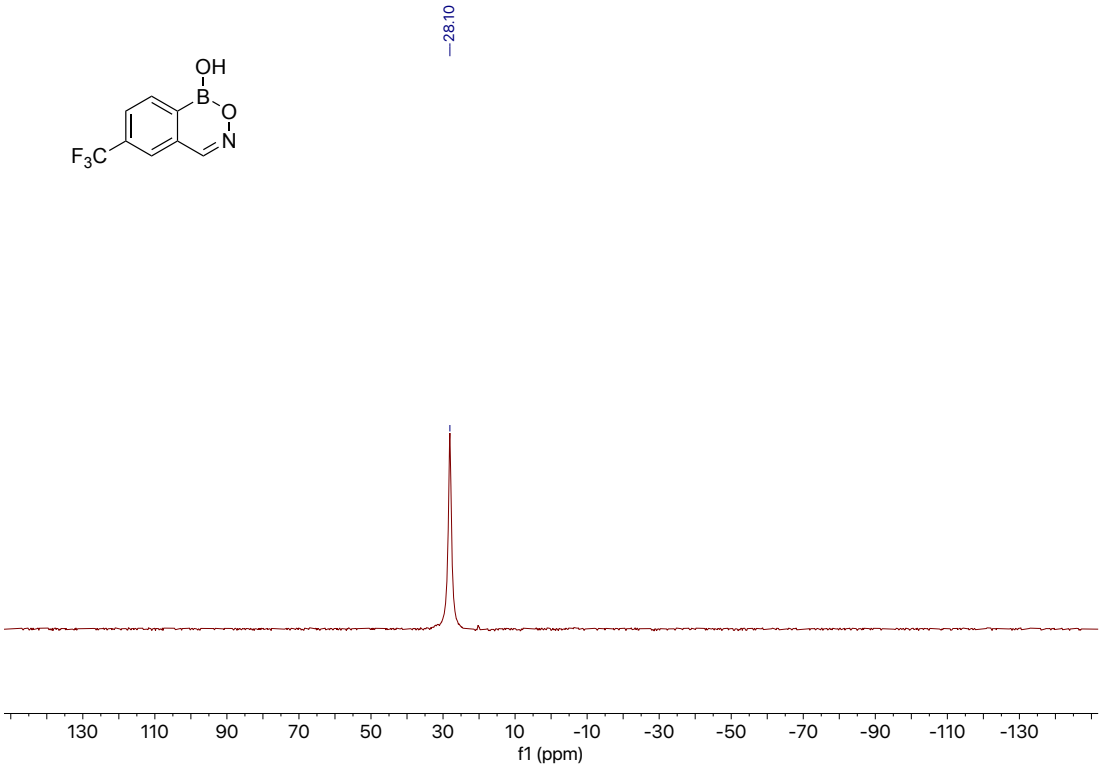


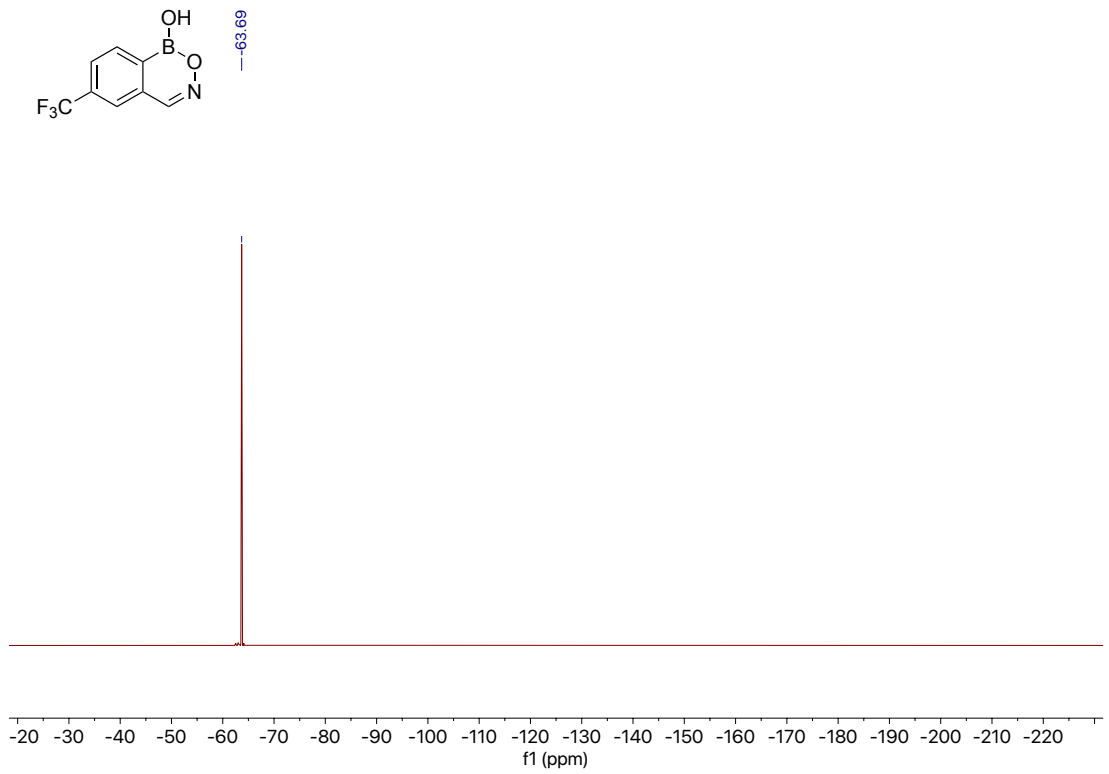


^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR for **6-(trifluoromethyl)-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1b)** in Acetone-d_6

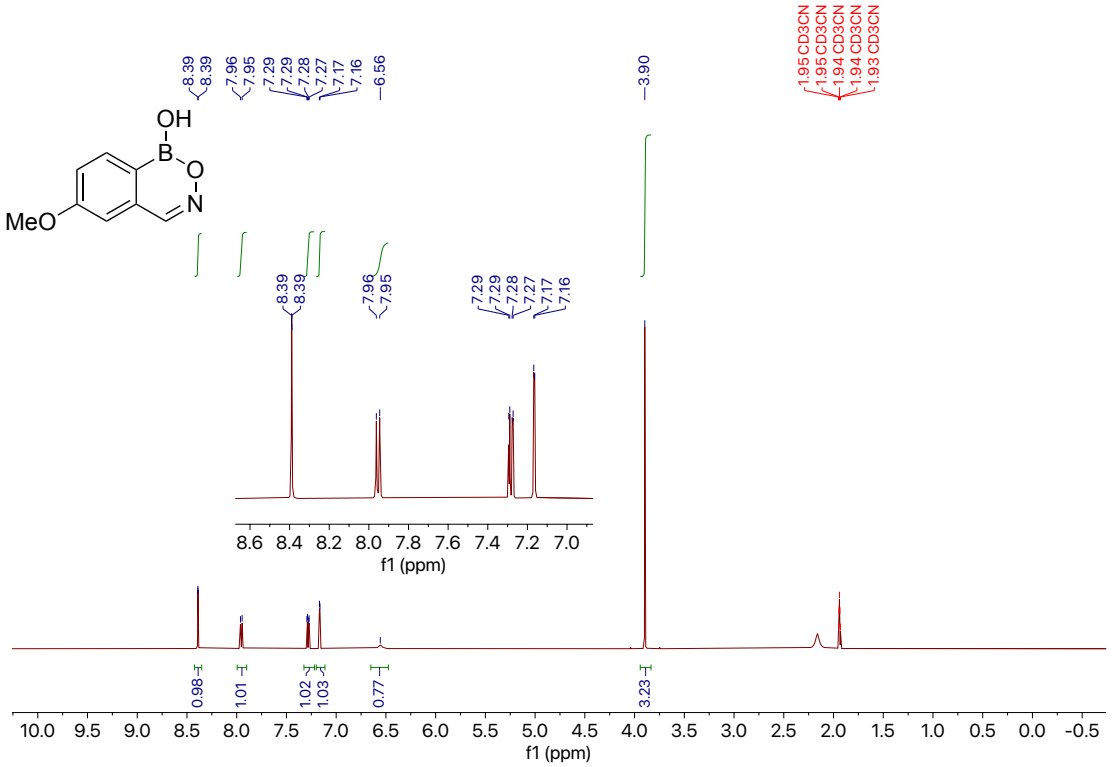


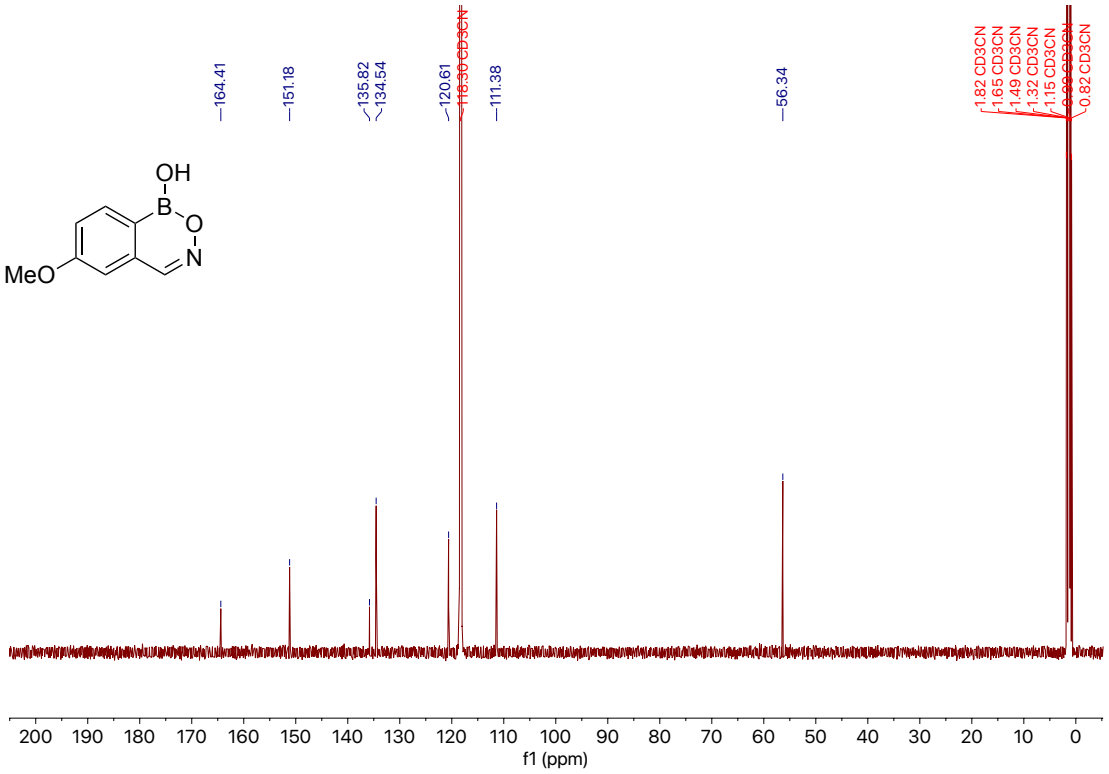

OH
B
O
N
F3C
206.26 Acetone
150.28
134.26
134.00
128.70
128.67
126.02
125.09
125.05
123.85
30.42 Acetone
30.36
30.27 Acetone
30.21
29.96 Acetone
29.80 Acetone
29.65 Acetone
29.49 Acetone
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

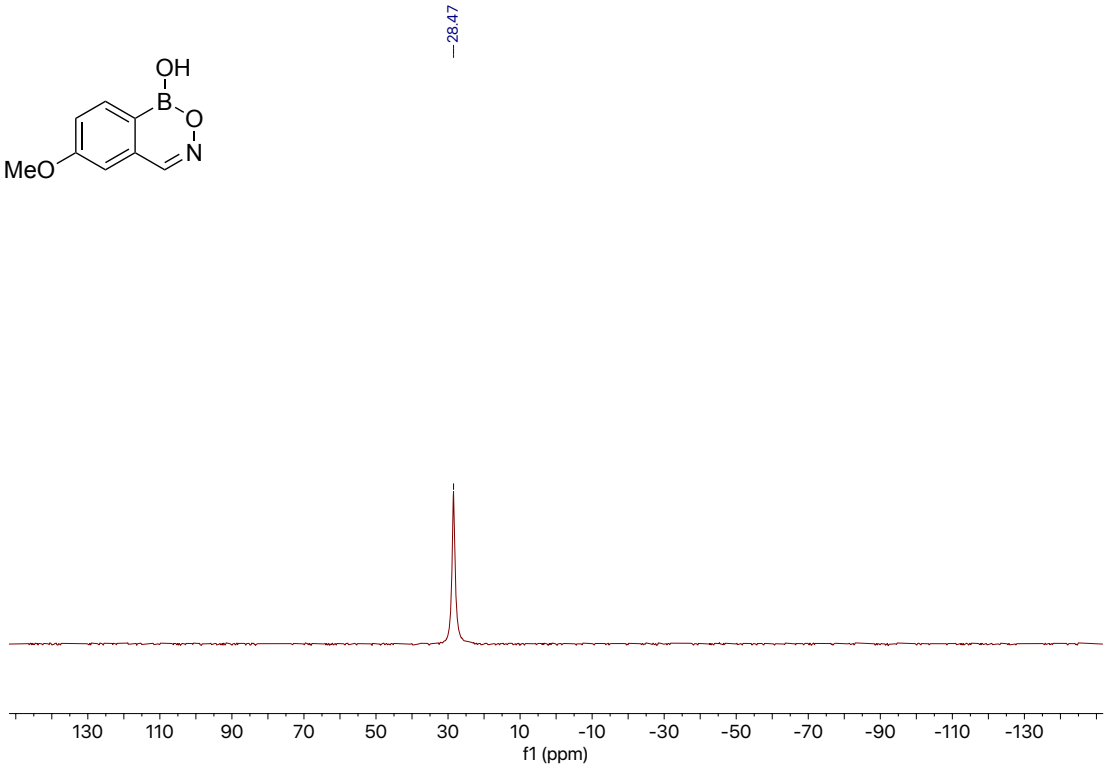

OH
B
O
N
F3C
28.10
130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130
f1 (ppm)



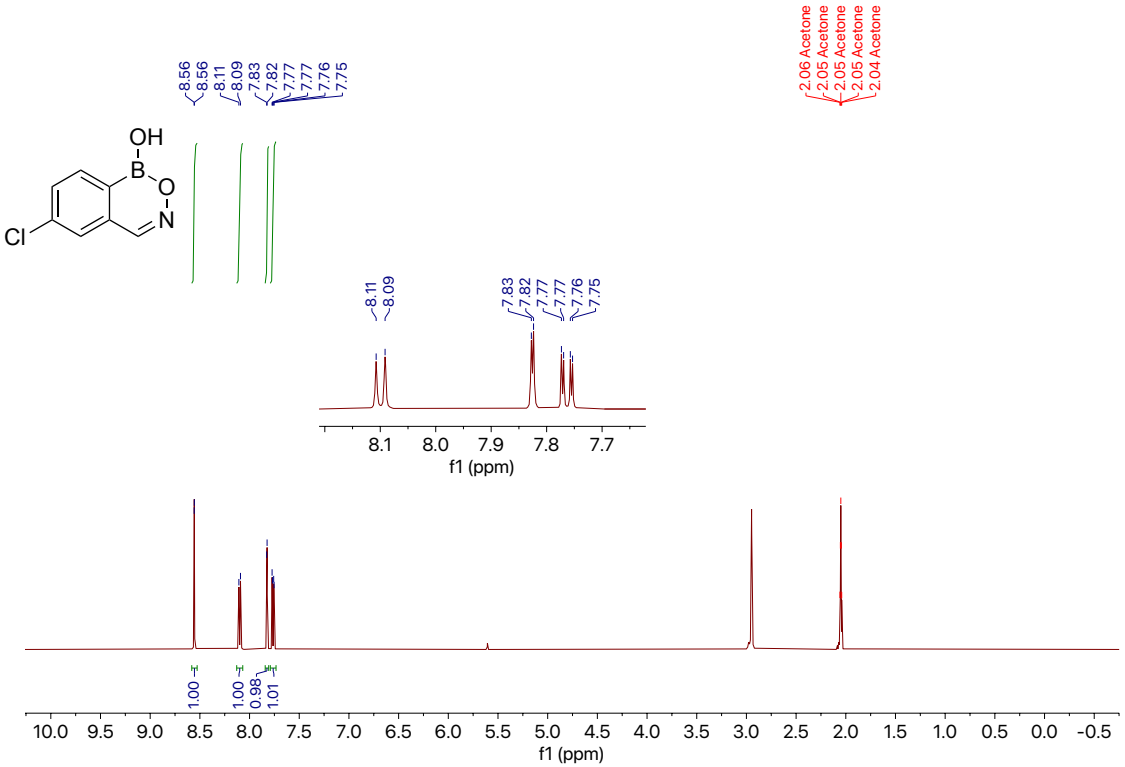
^{1}H, $^{13}C\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR for **6-methoxy-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1c)** in CD_3CN

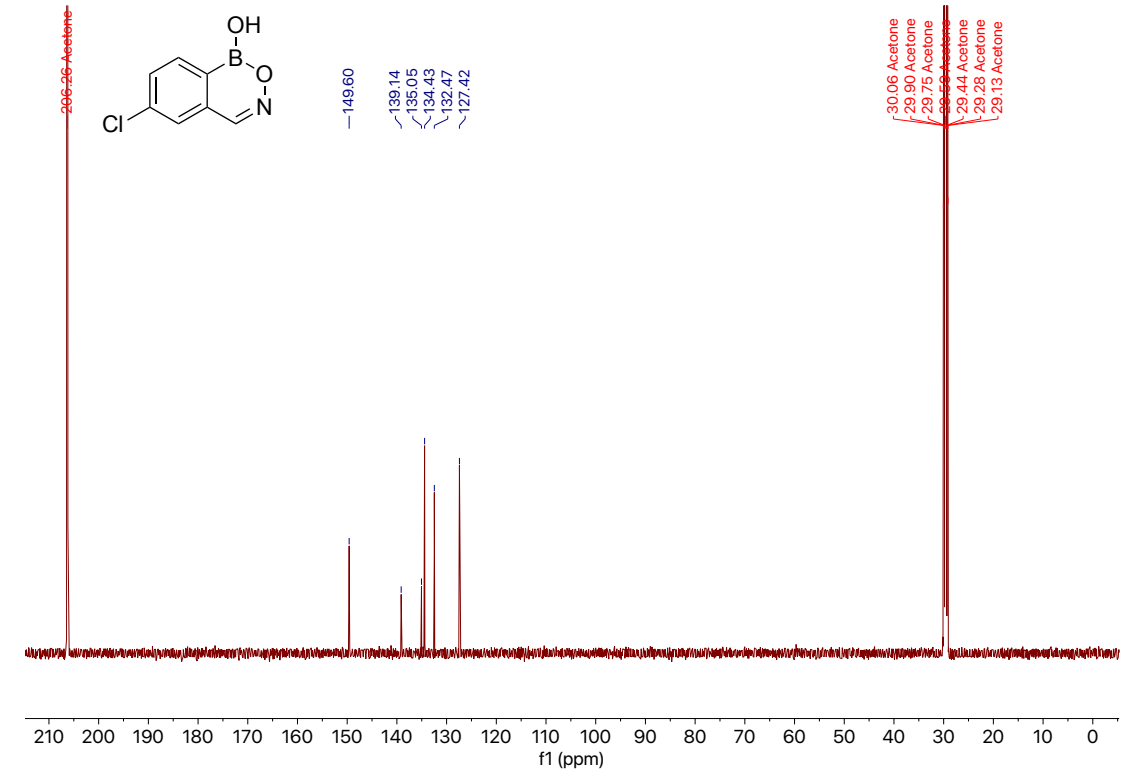


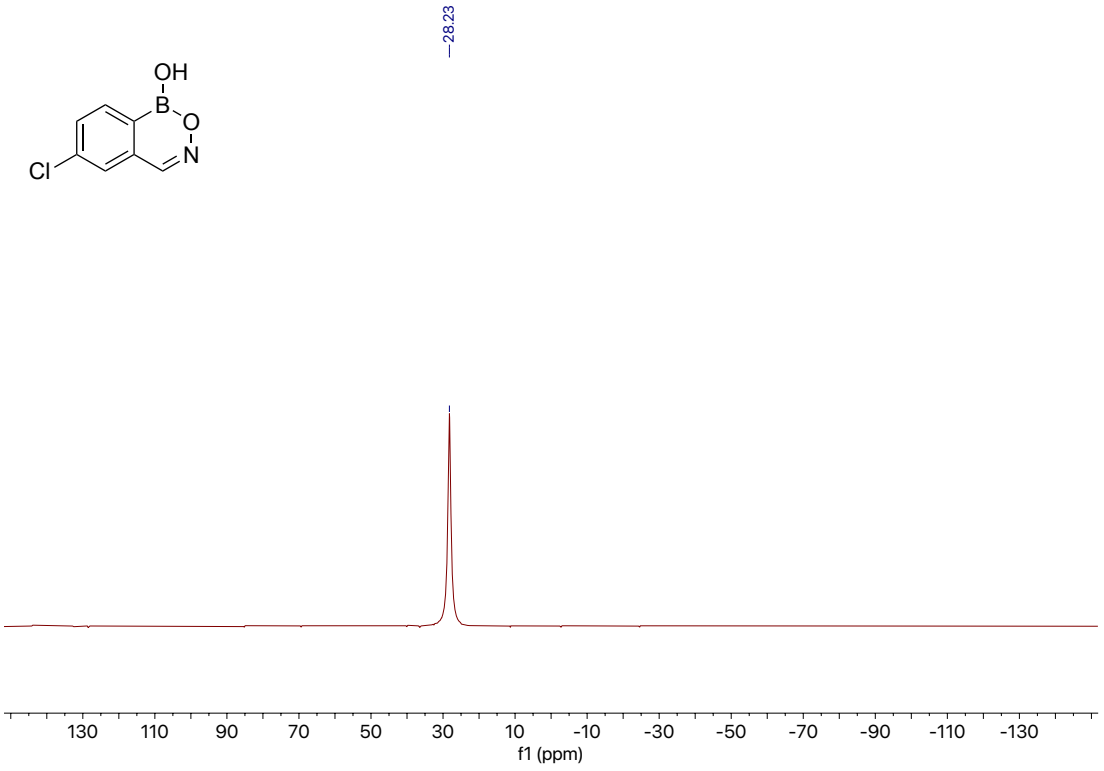

164.41
151.18
135.82
134.54
120.61
118.36 CD3CN
111.38
56.34
1.82 CD3CN
1.65 CD3CN
1.49 CD3CN
1.32 CD3CN
1.15 CD3CN
0.82 CD3CN
OH
B
O
N
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


28.47
OH
B
O
N
MeO
130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130
f1 (ppm)

^{1}H, $^{13}C\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR for **6-chloro-1H-benzo[d][1,2,6]oxazaborinin-1-ol (BAC 1d)** in Acetone-d_6






28.23
OH
B
O
N
Cl
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
f1 (ppm)

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